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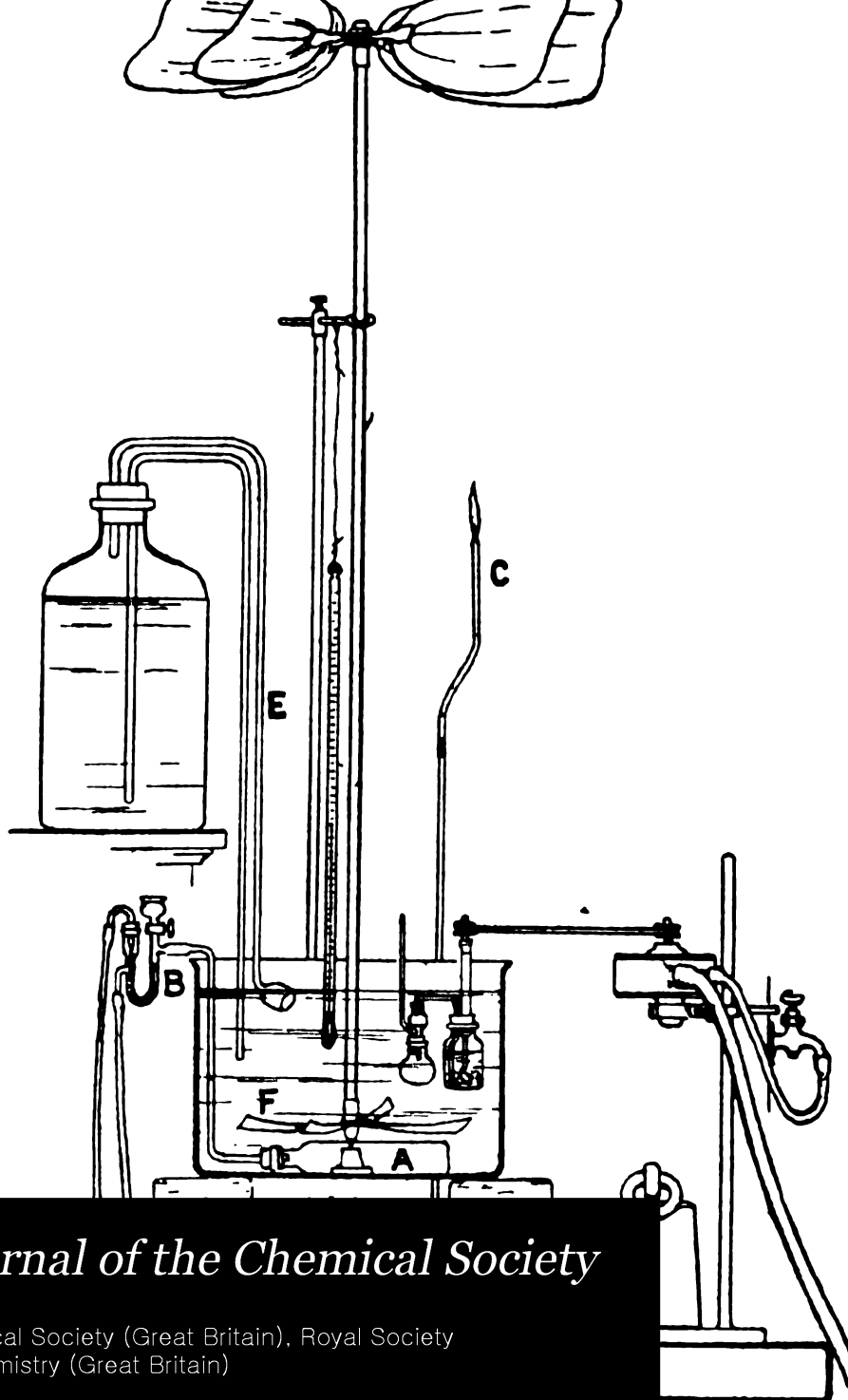
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# *Journal of the Chemical Society*

Chemical Society (Great Britain), Royal Society  
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	PAGE
CXLV.—The Action of Nitric Acid on Bromophenolic Compounds. By WILLIAM ROBERTSON, A.R.C.S.	1475
CXLVI.—Derivatives of Normal- and iso-Butyrylpyruvic Acids. By ARTHUR LAPWORTH and A. C. OSBORN HANN	1485
CXLVII.—Optically Active Esters of $\beta$ -Ketonic and $\beta$ -Aldehydic Acids. Part I. Menthyl Formylphenylacetate. By ARTHUR LAPWORTH and A. C. OSBORN HANN	1491
CXLVIII.—Optically Active Esters of $\beta$ -Ketonic and $\beta$ -Aldehydic Acids. Part II. Menthyl Acetoacetate. By A. LAPWORTH and A. C. OSBORN HANN	1499
CXLIX.—The Mutarotation of Camphorquinonehydrazone and Mechanism of Simple Desmotropic Change. By ARTHUR LAPWORTH and A. C. OSBORN HANN	1508
CL.—The Action of Sodamide and Acyl-substituted Sodamides on Organic Esters. By ARTHUR WALSH TITHERLEY, D.Sc., Ph.D.	1520
CLI.—3 : 5-Dichloro- <i>o</i> -xylene and 3 : 5-Dichloro- <i>o</i> -phthalic Acid. By ARTHUR WILLIAM CROSSLEY and HENRY RONDEL LE SUEUR	1533
CLII.—Non-existence of the Gaseous Sulphide of Carbon described by Deninger. By EDWARD JOHN RUSSELL and NORMAN SMITH	1538
CLIII.—Note on the Localisation of Phosphates in the Sugar Cane. By CHAS. HENRY GRAHAM SPRANKLING	1543
CLIV.—Isometric Anhydrous Sulphates of the Form $M''SO_4, R_2'SO_4$ . By FREDERIC R. MALLET	1546
CLV.—Asymmetric Optically Active Selenium Compounds and the Sexavalency of Selenium and Sulphur. <i>d</i> - and <i>l</i> -Phenylmethylselenetine Salts. By WILLIAM JACKSON POPE, F.R.S., and ALLEN NEVILLE, B.Sc.	1552
CLVI.—Hydroxyoxamides. Part II. By ROBERT HOWSON PICKARD, CHARLES ALLEN, WILLIAM AUDLEY BOWDLER and WILLIAM CARTER	1563
CLVII.—The Constituents of Commercial Chrysarobin. By HOOPER ALBERT DICKINSON JOWETT and CHARLES ETTY POTTER	1575
CLVIII.—The Constituents of an Essential Oil of Rue. By FREDERICK B. POWER and FREDERIC H. LEES	1585
CLIX.—Methyl $\beta$ -Methylhexyl Ketone. By FREDERIC HERBERT LEES	1594
CLX.—The Constitution of the Metallic Cyanides as Deduced from their Synthetic Interactions. The Constitution of Hydrogen Cyanide. By JOHN WADE, D.Sc.	1596

# JOURNAL OF THE CHEMICAL SOCIETY.

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## TRANSACTIONS.

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# JOURNAL OF THE CHEMICAL SOCIETY.

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## TRANSACTIONS.

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### I.—*The Oxidation of Sulphurous Acid to Dithionic Acid by Metallic Oxides.*

By H. C. H. CARPENTER.

THERE are, so far as I have been able to ascertain, only two metallic oxides which have been found to react with sulphurous acid and produce dithionic acid. These oxides are manganese dioxide and hydrated ferric oxide.

The object of the present research was the investigation of reactions which lead to the formation of dithionic acid, with particular precautions as to the purity of the sulphurous acid and the various oxides used. In this study, the author has been helped by the discovery that dithionic acid is obtained when sulphurous acid reacts with (a) manganic hydroxide,  $Mn_2O_3(OH)_2$ , and (b) cobaltic hydroxide,  $Co_2(OH)_6$ .

It is *a priori* possible in all cases for the 'available oxygen' in the metallic oxides to form either sulphuric acid or dithionic or both, as the following equations show :—



In the case of ferric hydroxide, Gelis (*Ann. Chim. Phys.*, 1862, [iii], 65, 222) states that the whole of the available oxygen goes first to dithionic acid. On the other hand, it has always been found in the investigations with manganese dioxide that a mixture of dithionic and sulphuric acids results.

Gelis's experiments with ferric hydroxide have been repeated by the author of this paper and his conclusion confirmed that a nearly theoretical yield of dithionic acid is obtained. Although it has not been

## 2 CARPENTER: THE OXIDATION OF SULPHUROUS ACID TO

found possible to obtain theoretical yields of this acid from the corresponding hydroxides of manganese, cobalt, or nickel, yet on account of the greater development of energy in the reduction of these oxides, there is very strong reason for believing that a partial or even complete decomposition of dithionous acid into sulphuric and sulphurous acids would take place. The facts which point to this conclusion are contained in the two following tables. The first shows the percentages of dithionous and sulphuric acids obtained from the four hydroxides already mentioned; the second indicates the changes of energy expressed in thermal units, involved in the reduction of the oxides:—

### I.

Hydroxide.	Percentage of dithionate.	Percentage of sulphate.
Ferric .....	96·06 ; 96·23	Not estimated.
Manganic.....	75·52 ; 74·53	25·42.
Cobaltic .....	36·97 ; 35·07	63·80 ; 63·33.
Nickelic .....	Nil.	101·04.

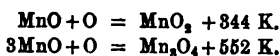
### II.

Reduction of the hydroxides.	Heat of reaction.
$\text{Fe}_2(\text{OH})_6 = 2\text{Fe}(\text{OH})_2 + \text{O} + \text{H}_2\text{O} \dots$	- 546 calories.*
$\text{Mn}_2(\text{OH})_6 = 2\text{Mn}(\text{OH})_2 + \text{O} + \text{H}_2\text{O} \dots$	- 448 „
$\text{Co}_2(\text{OH})_6 = 2\text{Co}(\text{OH})_2 + \text{O} + \text{H}_2\text{O} \dots$	- 225 „
$\text{Ni}_2(\text{OH})_6 = 2\text{Ni}(\text{OH})_2 + \text{O} + \text{H}_2\text{O} \dots$	+ 13 „

It will be seen, on comparing the two tables, that the greater the energy required for the reduction of the hydroxides, the larger is the

\* The value of this calorie is that of the unit K used by Ostwald. It is that quantity of heat which is given up by 1 gram of water as it cools from the boiling to the freezing point. The values quoted for the reductions of the hydroxides of iron, cobalt, and nickel have been taken from Ostwald's *Lehrbuch der allgemeinen Chemie*.

Thermal data relating to the oxide  $\text{Mn}_2\text{O}_3$  appear to be entirely lacking, and the figure given is only an approximate one, for purposes of comparison, obtained in the following way:



The mean of these values is taken to represent the heat of formation of manganic from manganous oxide.



This value refers to the oxide, not the hydroxide. Judging by the analogy of the difference between  $\text{MnO}$  and  $\text{Mn}(\text{OH})_2$ , the value for  $\text{Mn}_2(\text{OH})_6$  would be larger by 3 or 4 units in the middle figure, but either value serves quite well for the relation which it is desired to emphasise. The sesquioxides of iron, manganese, and cobalt thus show negative heats of reduction the values of which vary in the order mentioned, beginning with iron as the largest. In striking contrast to these, nickelic oxide shows a decided positive heat of reduction.

percentage yield of dithionous acid. The maximum yield is obtained with ferric hydroxide where the energy that needs to be supplied is such that it is possible to stop the reaction almost wholly at the stage represented by the equation



Whether the slight deficit from the theoretical number is due to a slight decomposition of the nature



or to a defect in the method of estimation used, is a question which it has not been found possible to decide.

In the case of manganic hydroxide, about one-fourth, and in the case of cobaltic hydroxide, about two-thirds, of the dithionous acid formed is decomposed in the manner indicated in equation (iv).

The reduction of nickelic hydroxide differs essentially from that of the other three in being an exothermic change, and the energy liberated is such that the reaction cannot be stopped at the intermediate stage, but proceeds wholly to the last stage, and the only oxidation product is sulphuric acid. The data in Table II are thus sufficient to account in a simple manner for the results obtained by the author which have been given in Table I, although the thermochemical values of the reactions between the four hydroxides and sulphurous acid are not known.

#### EXPERIMENTAL PART.

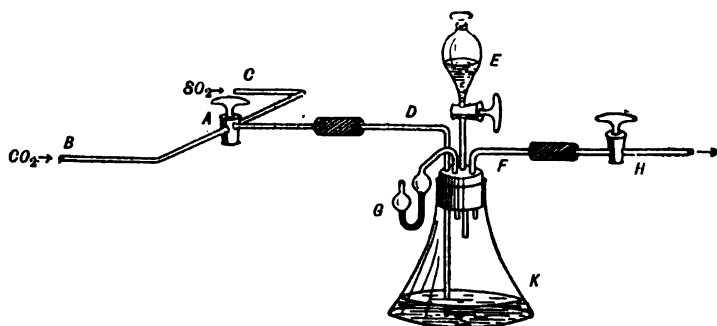
The essential part of the apparatus used in the author's experiments will be found in the diagram on p. 4.

*A* is a three-way cock in a T-tube bent at right angles in the manner indicated. The two arms can be connected, that at *B* with an apparatus evolving carbon dioxide, that at *C* with an apparatus giving off sulphur dioxide. At the other end, the T-piece is connected by thick rubber tubing with the flask, *K*, in which the reaction takes place. The flask has a capacity of about 300 c.c. and its neck is fitted with a rubber cork bored with four holes. Through these pass—

- (i) The tube delivering the gas either from *B* or *C*.
- (ii) The exit tube, *F*, which is further connected with the stopcock, *H*.
- (iii) A small mercury pressure-gauge, *G*.
- (iv) A dropping funnel, *E*, which becomes necessary when it is desired to estimate the sulphuric acid formed in the reaction.

The apparatus was tested in the following way to see whether a solution of sulphurous acid, free from sulphuric acid, could be obtained in the flask, *K*.

It was fitted together in the manner indicated, except that neither the gauge nor the dropping funnel was fitted into the cock, the holes being temporarily plugged with glass rods, and further that the stop-cock, *H*, was not fitted on to the exit tube, *F*. About 200 c.c. of distilled water were placed in the flask and a quick current of carbon dioxide was sent through to displace the air from the apparatus, the water being boiled steadily, but not too rapidly. The carbon dioxide was evolved by heating pure sodium hydrogen carbonate carefully packed in a glass tube placed in a gas furnace. It was found that after  $1\frac{1}{2}$ —2 hours the limit of air displacement possible by this method had been reached, but a slight froth, unabsorbed by potassium hydroxide solution, always remained. When this was the case, the water in the flask was gradually cooled, first by water and then by ice, the current of gas being maintained. From 75—100 c.c. of water remained. The cock, *H*, was now attached and when the air had been expelled it was closed. The



first of the plugs in the cork was next removed, the dropping funnel inserted, its air displaced, the tap closed, and a stopper placed in the neck. Lastly, the second plug was taken out, the empty gauge put in, and after the expulsion of its air, mercury poured in. By this time the water, which had a temperature of about  $5^{\circ}$ , was generally saturated with carbon dioxide, so that when the cock, *A*, was turned, isolating the apparatus from the arm, *B*, and connecting the latter with *C*, only at most a slight diminution of pressure inside the apparatus was noticed on standing; carbon dioxide was passed through the tube, *C*, until it had displaced all the air. The pressure can, of course, always be increased again by connecting the apparatus with *B* for a few seconds.

Meantime, during the last 20—30 minutes, a solution of sodium hydroxide previously saturated with sulphur dioxide had been slowly warmed in a flask provided with a leading tube, in order to expel the air by a gentle but steady current of gas. When all the air had been

removed, the apparatus was attached to *C*, the cock, *A*, quickly turned so that the gas passed into the flask, *K*, the cock, *H*, opened, and the arm, *B*, disconnected from the sodium hydrogen carbonate tube. Sulphur dioxide now passed through the water contained in the flask, gradually saturating it.

In the meantime, a solution of barium chloride in water acidified with hydrochloric acid had been steadily boiling in an open flask for  $1\frac{1}{2}$ —2 hours to expel dissolved air. The solution was then rapidly transferred to the dropping funnel. There it was cooled to the ordinary temperature in a stream of carbon dioxide and the current maintained up to the moment when the solution was run into the flask. This was done after sulphur dioxide had been passing in for  $1\frac{1}{2}$  hours, care being taken that the tap was turned off before the last c.c. of liquid could run through. No turbidity of the liquid in the flask could be detected. When, after shutting the cocks at *A* and *H* and isolating the apparatus, a pressure from within was registered by the mercury gauge, the apparatus was permanently isolated between *A* and *H* and at the same time the flask allowed gradually to regain the laboratory temperature. This ensured a steady pressure of sulphur dioxide from within, the gas forcing its way through the gauge. Even after 18 hours no precipitate had formed, and it was accordingly concluded that the method was successful in giving a solution of sulphurous acid free from sulphuric acid. This test was sufficient for the purpose of the experiments, although solutions of sulphurous acid under the influence of diffused light, gradually undergo a chemical change which is not yet understood.

It should be mentioned that both the carbon dioxide and sulphur dioxide were passed through a small empty wash bottle, where the greater part of the water given off with them was retained, before entering the T-piece at *B* and *C* respectively. The method of obtaining sulphur dioxide described is very convenient; a continuous stream for 10 hours may, by carefully regulating the heating, be obtained from about 3 litres of saturated sodium hydrogen sulphite solution.

Separate experiments were needed for the estimation of dithionous and sulphuric acids formed in the reaction between a metallic oxide and sulphurous acid.

#### *Estimation of the Sulphuric Acid.*

The method is very similar to that adopted when the solution of sulphurous acid was tested for the presence of sulphuric acid. In the experiments with the dried metallic oxides, which it was desired to keep in a compact state, the latter were put into the



flask, *K*, by momentarily removing the rubber-cork and then replacing it at the stage where the water had already been boiled and was cooled in ice, a steady current of carbon dioxide being all the while maintained. On the other hand, in those with the moist hydrated oxides in a fine state of division, known volumes of these, suspended in water, were introduced by a pipette into the flask at the beginning of the experiment instead of distilled water alone.

After the reaction with sulphurous acid was finished, the sulphuric acid was estimated in the flask in which the reaction had taken place, to avoid the oxidation of the dissolved sulphurous acid. The liquid was precipitated by an acidified barium chloride solution in the manner already described and was allowed to stand until it had clarified. The supernatant liquid was poured off through a weighed filter and the precipitate repeatedly washed by decantation, first with an air-free, dilute solution of hydrochloric acid and afterwards with distilled water, and the estimate of the barium sulphate carried out in the usual way.

#### *Estimation of the Dithioni Acid.*

In this case, except that the dropping funnel is not needed, the method is the same as the foregoing one up to the point where the action of sulphurous acid on the hydroxide is complete. A thermometer dipping below the surface of the liquid was substituted for the dropping funnel. A stream of carbon dioxide was then passed through the liquid, which was gradually warmed until it had acquired a temperature not exceeding 45°\* and well shaken in order to expel as much of the dissolved sulphur dioxide as possible. After cooling in a current of the same gas, it was precipitated with an excess of a warm saturated barium hydroxide solution. In this way, sulphurous and sulphuric acids were removed whilst a solution of barium dithionate and the excess of barium hydroxide remained. The precipitate was allowed to settle, the liquid poured off through a filter, and the residue washed six times with boiling water by decantation, the washings being successively added to the main filtrate. The barium hydroxide was then precipitated with carbon dioxide at 100°, filtered, and the filtrate evaporated on a steam bath to dryness on account of a small quantity of barium carbonate which always remains dissolved. The residue was extracted six times with hot water and the solution of barium dithionate thus obtained filtered into a weighed platinum dish. It was evaporated to dryness on the steam-bath and ignited until the weight was constant.

\* At temperatures above 50°, solutions of the dithionates of iron, cobalt, and nickel begin to decompose into the corresponding sulphates and sulphurous acid.

In the estimations of dithionic acid resulting from cobaltic hydroxide, which contained a small quantity of alkali, the barium dithionate solution was at the last stage converted into barium sulphate by prolonged boiling in a reflux apparatus with a few drops of hydrochloric acid solution. This modification is necessary, but not so convenient as the other method.

The disadvantage attaching to this method of estimating dithionic acid is that it involves the washing out of a small quantity of barium dithionate from a large quantity of barium sulphate, with consequently a possible loss of the dissolved salt by adsorption. This applies to the acid as obtained from the hydroxides of iron and cobalt where the reduction is slow and the amount of sulphurous acid used is large, but not to the other two cases where the reduction is rapid and the quantity of sulphurous acid used is small.

*Estimation of the 'Available' Oxygen in the Metallic Oxides.*

Ferric hydroxide was estimated gravimetrically as ferric oxide. The other three oxides were made to react with an excess of standard oxalic acid, which was afterwards titrated with standard potassium permanganate solution, and in this way their available oxygen determined. Owing to the influence of light on solutions of oxalic acid, the latter were always freshly prepared, immediately before they were needed, from pure ammonium oxalate, which can easily be obtained and keeps well. The potassium permanganate solutions were standardised against this.

For the estimations of available oxygen in the moist precipitates, the method of withdrawing a known volume by a pipette was used here just as in the estimations of dithionic and sulphuric acids.

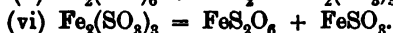
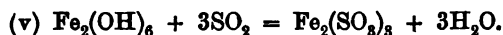
It was not found that the pink colour of the cobalt solutions or the green colour of the nickel solutions interfered with the permanganate titrations or masked the colour of the permanganate. Seeing that these colours were complementary, the plan was tried of decolorising whichever liquid was being titrated with a few drops of a solution of the sulphate of the other metal, but in neither case was any effect on the results noticeable.

Particulars of the methods adopted for the preparation of the metallic hydroxides will be found in the sections dealing with the reduction of each oxide. The specimens referred to as 'moist' were kept in closed vessels and suspended in water or, in the case of nickelic hydroxide, in dilute alkali. For the estimations, a measured volume was withdrawn by a pipette after the liquid had been thoroughly shaken to ensure a uniform distribution of the solid. Any portion of the latter adhering to the walls of the pipette was afterwards washed in. The 'dried' specimens were obtained from the 'moist' by allowing the latter to dry gradually

on clean porous plates. On drying, the precipitate shrinks and as a rule becomes completely detached from the plate, or needs at most only a slight touch to loosen it. After removing it, the surface of the plate is found to be traced with a delicate pattern resembling vegetable cell-structures in a remarkable degree. Here and there, spirals are formed, caused by the precipitate having adhered with varying degrees of intensity to the plate. These facts were noticed with all the precipitates dried in this way.

*Reduction of Ferric Hydroxide. Formation of Ferrous Dithionate.*

Gelis (*loc. cit.*) claims to have proved that the reaction between ferric hydroxide and sulphurous acid takes place in the following way:—



He found that when a current of sulphur dioxide is passed into water containing ferric hydroxide in suspension, the latter dissolves and a liquid is obtained which has a red colour, an acid reaction, and a strong odour of sulphur dioxide, and concluded from his analyses that neutral ferric sulphite,  $\text{Fe}_2(\text{SO}_3)_3$ , is formed.

When the solution has stood for some hours in a closed vessel, the red colour is found to have changed to pale green. The analytical results quoted show that ferrous dithionate and ferrous sulphite have been formed in approximately equal and quantitative amounts as shown in equation (vi). A small, but not negligible, quantity of ferrous sulphate was shown to be also present. Gelis regarded this as an accidental product, probably due to the oxidation of some of the sulphite by the air.

It is curious that so remarkable an oxidation of sulphurous acid, from which, according to the explanation given, no sulphuric acid, but solely dithionic acid, results, should have apparently attracted no attention. Gelis's work, published 39 years ago, has never been repeated, and yet certain criticisms obviously suggest themselves to anyone who studies the paper referred to.

It is, in the first place, noteworthy that the specimens of iron used in those experiments do not appear to have been tested for the presence of manganese, and there can be hardly any doubt that small quantities of this metal were present. It is a natural question to ask whether this impurity may not really have been the cause of the formation of dithionic acid, possibly by acting catalytically. In the second place, the question whether sulphuric acid is formed or not cannot be dismissed in the manner indicated, but must, if possible, be tested by experiment.

It is evident that no pains were taken to exclude air from the apparatus and liquids used, but this is one of the fundamental conditions which must be realised if this point is to be settled.

In my own experiments, the ferric hydroxide was prepared in the following way. The ferric chloride used was purified by separating iron as the basic formate and repeating the precipitation until it was quite free from the last traces of manganese. This was held to be the case when fusion of the ferric formate with potassium nitrate and sodium carbonate yielded a product from which the green tint of a manganate was entirely absent, and this test was usually satisfied after the third precipitation of the iron. Separation by the formate is much quicker than by either the acetate or succinate. The precipitate of basic ferric formate breaks up, on warming, into a very fine powder, which can be thoroughly well washed with boiling water by decantation, and settles quickly. When pure, it was dissolved in hydrochloric acid, precipitated with ammonia, and the hydroxide washed until it was so finely divided that it remained for several days suspended in the liquid.

The reduction of such ferric hydroxide by sulphurous acid is very slow and I can by no means confirm Gelis's statement that the substance dissolves in that quantity of the acid corresponding to the formation of the neutral sulphite of iron. To take an example, 0.2859 gram of ferric hydroxide suspended in water was acted upon by a current of sulphur dioxide for  $7\frac{1}{2}$  hours. The liquid was repeatedly shaken, but even after  $3\frac{1}{2}$  days 0.1041 gram of hydroxide still remained—indeed the analytical results quoted for iron were, in both cases, derived from experiments in which the residual ferric hydroxide had to be estimated. This was done by filtering it off just before the precipitation with barium hydroxide. The precipitate was well washed, the washings being added to the main filtrate, and ignited until the weight was constant.

The reason why Gelis found ferric hydroxide dissolved readily in sulphurous acid probably was that the substance was not thoroughly washed. Freshly precipitated and unwashed ferric hydroxide is very quickly dissolved by sulphurous acid. The more pains that are taken to wash out adhering salts, the slower does the reaction become, until a condition is reached similar to that of which an instance has already been given. In such a case, the liquid begins to acquire a yellow colour after 4—5 hours, and this increases somewhat in intensity if the current of gas is maintained, but a red solution has not been obtained. After standing 12—18 hours, the yellow colour changes to pale green and the solution evidently contains iron in the ferrous state. The dithionous acid which has been formed may then be estimated. The results already quoted show that its formation is quite independent of

the presence of manganese. They also show that less than 4 per cent. of the dithionic acid formed undergoes any decomposition. Whether this slight decomposition takes place has not been actually decided. The fact that some unchanged ferric hydroxide always remained in the liquid rendered it impossible to test for the presence of sulphuric acid. When an acidified solution of barium chloride was introduced, with the needful precautions, into the flask, no precipitate was noticeable for a few seconds, and in one case for nearly a minute, but after this interval a turbidity could always be detected, and this gradually increased in intensity. This can be accounted for by the diffusion through the liquid of the hydrochloric acid introduced and its reaction with the ferric hydroxide. The ferric chloride formed would react with the sulphurous acid present, oxidising it, as is well known, to sulphuric acid, and this would be precipitated by the barium chloride present. There can, however, be little hesitation in concluding that if any sulphuric acid is formed in the reaction, it can only be a minute quantity.

Enough has been said to show that there can be no question of testing Gelis's first equation with ferric hydroxide which has been thoroughly washed. The author's experiments, however, agree with those of Gelis in showing that there is a stage of the reaction preceding that of ferrous dithionate and ferrous sulphite, corresponding probably to the formation of a ferric sulphite. Evidence of a similar stage has been obtained, although to a less degree, in the experiments with cobaltic hydroxide, but not with the other two oxides.

*Reduction of Manganic Hydroxide,  $Mn_2O_3(OH)_2$ . Formation of Manganous Dithionate and Manganous Sulphate.*

The reduction of this hydroxide stands in sharp contrast with that of ferric hydroxide. It takes place with the utmost ease and this is the more remarkable because previous investigators have concluded that exactly the opposite is the case. Heeren (*Pogg. Ann.*, 1826, 7, 55), discussing the formation of sulphuric acid in the reaction between manganese dioxide and sulphurous acid, quotes Berzelius to the effect that if the dioxide contains no manganic hydroxide, the sole product is manganous dithionate; but that as this impurity is nearly always present, a certain quantity of sulphate is also formed. After questioning whether this statement is founded on direct experiment, Heeren gives analytical results to show that some of the sulphuric acid must be formed from the manganese dioxide, and even calculates how much has come from this on the assumption that the manganic hydroxide cannot give rise to any dithionic acid. He investigated the action of sulphurous acid on manganic oxides of various states of aggregation

and found it to be very slow except with precipitated specimens. He noticed that small quantities of dithionic acid were formed, but suggests that they were due to some of the dioxide being present. So far from this being the case, the yields of dithionic acid obtained by the author from manganic hydroxide are higher by more than 5 per cent. than the highest obtained by Spring and Bourgeois (*Bull. Soc. Chim.*, 1886, [ii], 46, 151) in their investigation of the yields obtained from manganese dioxide in different states of aggregation. An even greater percentage of dithionic acid was obtained by using manganic hydroxide which had been dried at  $100^{\circ}$  and thus assumed a more compact state. This was evident from the fact that it took fully 30 times as long to dissolve in sulphurous acid as the undried specimen.

In preparing the oxide for these experiments, a specimen of manganous nitrate containing only a very small quantity of iron was used. The latter was first removed as basic ferric formate. The manganese was then precipitated with ammonia and bromine, and the hydrated dioxide thoroughly washed with nitric acid and then with water. In preparing manganic hydroxide from this, the directions given by Carius (*Annalen*, 1856, 98, 53) were followed exactly.

The reduction of the 'moist' oxide by sulphurous acid is very rapid, 0.25 gram, the amount usually treated, dissolving after about one minute's passage of the gas through the liquid. The estimation of the dithionic or sulphuric acid can be proceeded with at once. There is no evidence of the intermediate formation of a sulphite.

*Reduction of Cobaltic Hydroxide. Formation of Cobaltous Dithionate and Cobaltous Sulphate.*

The cobalt nitrate used for the preparation of the oxide was first freed from a small quantity of iron present by precipitating the latter as basic ferric formate. It was then purified by converting it into potassium cobaltinitrite. The latter, after being carefully washed, was dissolved in hydrochloric acid, and afterwards precipitated with the necessary precautions by bromine and potassium hydroxide. It was repeatedly washed, first with potassium hydroxide and afterwards with hot water. It is well known that the hydroxide thus obtained does not correspond to the formula  $\text{Co}_2(\text{OH})_6$ . The amount of available oxygen it contains depends on the exact conditions of its preparation. Further, it contains alkali, which cannot be removed without decomposing the hydroxide. On account of these facts, the percentage of available oxygen was estimated by oxalic acid in the manner already described.

For the complete reduction of about 0.25 gram of the 'moist' hydroxide, approximately 5 hours are needed. The liquid acquires a brown

colour, which gives place to light yellow as the solution of the hydroxide proceeds, and this in its turn is replaced by the pink colour characteristic of cobaltous salts. The liquid is then ready for the estimation of the dithionic and sulphuric acids formed.

In order to test whether the percentage of dithionic acid could be increased by retarding the rate of the reaction, a number of experiments were made with specimens of the hydroxide of different degrees of compactness. The results are illustrated in the subjoined table :

Condition of the hydroxide.	Approximate time of reduction of 0.25 gram.	Percentage of dithionic acid.
(i) Moist .....	5 hours	36.97 ; 35.07
(ii) Dried at 140—150° and finely powdered .....	4 days	28.14
(iii) Dried at 140—150° and coarsely powdered .....	5 „	23.41
(iv) Dried at 140—150°, but not powdered .....	6 „	10.87

In experiments ii, iii, and iv, a current of sulphurous acid was passed through the liquids for about 7 hours. At the end of 2 days, the current was renewed for a further period of 2 hours on account of the gauge registering a gradual diminution of pressure inside the apparatus. In these three cases, no colour, except the pink of cobaltous salts, was noticed during the reduction.

A comparison of the figures shows that the amount of decomposition of dithionic acid is increased by rendering the hydroxide more compact. This fact is accounted for, if it is borne in mind that in these cases, where reaction is taking place at the surface of solid particles, local heating is bound to take place, and the effect of such a cause upon dithionic acid is easily comprehended.

In the reductions of cobaltic hydroxide and ferric hydroxide, where a prolonged current of sulphur dioxide is necessary, care must be taken that the temperature of the liquid is kept just above the point at which the solid hydrate,  $\text{SO}_2 \cdot x\text{H}_2\text{O}$ , crystallises out ( $8^\circ$ ), otherwise the tube in the flask where the gas enters becomes choked.

#### *Reduction of Nickelic Hydroxide. Formation of Nickelous Sulphate.*

Preliminary experiments with this hydroxide had shown that both dithionic and sulphuric acids are produced by reduction with sulphurous acid, but when the estimations with the hydroxide obtained in as pure a state as possible came to be carried out, it was found that sulphuric acid is the sole product of the oxidation of the sulphurous acid used.

The nickelic hydroxide was prepared from a specimen of nickel nitrate containing a minute quantity of cobalt. The latter metal was removed as potassium cobaltinitrite. The filtrate was boiled with excess of hydrochloric acid, precipitated with potassium hydroxide, filtered, well washed, and then redissolved in hydrochloric acid. From this solution, it was precipitated with bromine and potassium hydroxide and in consequence of the readiness with which it loses oxygen in presence of water, it was washed with cold alkali only. In order to keep the moist hydroxide in an alkaline medium until the moment of its reaction with sulphurous acid, nitrogen was used instead of carbon dioxide to displace the air from the apparatus and liquids used. Further, as it is not safe to expose the hydroxide to a temperature of  $100^{\circ}$ , a modification of the methods of estimation of dithionous and sulphuric acids was necessary. After the expulsion of the air from the apparatus by nitrogen, and while the gas was still passing through, one of the glass plugs was removed and the cold liquid containing the hydroxide in suspension introduced by a pipette. The plug was then re-inserted and the usual course of the determination followed.

The reaction between this hydroxide and sulphurous acid is the most rapid of the four investigated. The absorption of the gas is so energetic that unless a very quick evolution is taking place at the moment when it is admitted into the apparatus, the liquid and precipitate in the flask are sucked back into the tube, *C*. The green colour of the nickalous salt is seen almost immediately.

The rate can be considerably diminished by increasing the size of the particles of the hydroxide and thus exposing relatively less surface. This was done by drying the substance at the ordinary temperature on a porous plate. Experiments were made with these dried specimens, both powdered and not powdered, in which the duration of the reaction was between ten and twenty minutes. But in none of these cases has any dithionous acid been detected, and this negative result has been confirmed for the moist hydroxide by the finding of rather more than the theoretical percentage for sulphuric acid.

*Note on the Action of Sulphurous Acid on the Dithionates of Lead and Barium.*

The only account of any experiments performed with the object of testing whether dithionous acid is obtained by the action of sulphurous acid on the peroxides of lead and barium is to be found in the paper of Gay Lussac and Welter (*Ann. Chim. Phys.*, 1818, 10, 312), where they describe the discovery of this acid. Their results were negative.



The author has made a number of experiments with these oxides in the apparatus described at an early stage of this paper, but has never found that any dithionic acid is produced. In view of the negative character of these results, the action of sulphurous acid on the dithionates of these metals was studied. It was found that solutions of barium dithionate are quite unaltered except at a temperature at which the influence of heat alone begins to be seen, when a gradual decomposition into barium sulphate [and sulphur dioxide sets in. On the other hand, solutions of lead dithionate are decomposed instantaneously, even at 5°, lead sulphite being precipitated and free dithionic acid remaining dissolved.

The experiments were carried out in a similar manner to those already described, the solid dithionates being introduced into the flask, *K*, after the water had been cooled in a stream of carbon dioxide. In the case of the decomposition of lead dithionate, the precipitate was filtered off and washed with air-free water. It dissolved completely in aqueous hydrochloric acid and liberated sulphur dioxide, which was recognised by its odour and the reduction of chromate paper. The filtrate was rendered alkaline with barium hydroxide and barium dithionate obtained after the removal of sulphurous and carbonic acids.

In conclusion, the author acknowledges with great pleasure the assistance of Mr. F. H. Palmer in the preliminary experiments with nickelic hydroxide and the dithionates of lead and barium, and of Mr. C. W. May in those with manganic hydroxide.

*Addendum.*—This paper had been placed in the hands of the Secretaries of the Chemical Society before the publication of the paper, by Julius Meyer, on the formation of dithionic acid (*Ber.*, 1901, 34, 3606). The ground covered in the two papers is very nearly the same.

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## II.—*The Production of hitherto unknown Metallic Borides.*

By SAMUEL AUCHMUTY TUCKER, Ph.B., and HERBERT R.  
MOODY, B.S., M.A.

UNTIL the electric furnace made their formation comparatively easy, the borides were almost unknown and even now there have not as yet been reports concerning many of them. Moissan has described a few of these compounds, notably those of iron, cobalt, nickel, carbon, calcium, strontium, barium, and, lately, silicon.

So far as they have been investigated, the borides present evidence of definite composition and crystallisation, they are stable and fuse at comparatively high temperatures. As a consequence of their high fusing point, hardness, and good crystallisation, it is quite possible that some of them may prove to have industrial uses.

The available processes for the production of borides are two in number. In the first, the two elements are heated together in the electric furnace, and in the second, boron chloride is passed over the metallic element. The former of these was selected as being the most practicable for the preparation of the borides described in this paper. The utmost care was taken to prevent the addition of carbon, silicon, &c., to the product in each case, and in our opinion the borides described were entirely free from these elements. The boron in each case was determined directly by Gooch's method (*Amer. Chem. J.*, 1887, 9, 23).

*Zirconium Boride.*—The zirconium salt available for the preparation of this boride happened to be the nitrate. In order to reduce this to the elementary state, two processes were tried.

In the first, the nitrate was ignited until it was wholly converted to the oxide. This was then subjected to the regular Goldschmidt process, which did not prove to be satisfactory.

In the second, the nitrate was dissolved in cold water and the hydroxide precipitated from this solution by sodium hydroxide. Cold water was used in washing the precipitate, inasmuch [as hot water causes it to become insoluble. After being washed, the hydroxide was dissolved in hydrofluoric acid and to this solution neutral potassium fluoride solution was added, forming a precipitate of the double fluoride,  $3KF, ZrF_4$ . When dry, this salt was reduced by means of powdered aluminium and the cake thus formed was boiled for three days with concentrated hydrochloric acid. It was found impossible to filter the product rapidly, even with the aid of suction. After being washed with hot water, the metal was ready for use.

The elementary boron was prepared by fusing boric acid and reducing the oxide thus formed with metallic magnesium. To remove magnesium salts, the cooled mass was boiled with dilute hydrochloric acid, filtered, washed, and then boiled for three days with hydrochloric acid of sp. gr. 1.2. After filtering and washing, the residue was boiled for several hours with hydrofluoric acid, and after a final washing it was dried.

For preparing the zirconium boride, 15 grams of the zirconium were mixed with 2.2 grams of boron and the whole heated for 5 minutes in a carbon crucible with the aid of a current of 200 amperes and 65 volts. The product was a button, blackish on the outside, brittle, and of a steel grey colour on fracture. Under the microscope, it proved to

be an agglomeration of brilliant, tabular, translucent to transparent crystals, many of these being colourless. It had a sp. gr. 3.7 and a hardness 8. It was slowly attacked by hot concentrated acids and aqua regia. Boiling liquid bromine attacked it feebly.

Analyses of the compound were made and 86 per cent. of zirconium was found to be present. This corresponds very closely with the theoretical amount of zirconium in a boride in which zirconium is quadrivalent; therefore the formula of this compound is undoubtedly  $Zr_3B_4$ .

*Chromium Boride.*—This boride was made by heating a charge consisting of 10 grams of metallic chromium and 2.1 grams of boron for 6 minutes by the aid of a current of 175 amperes and 60 volts. The product was a well formed button, greenish on the outside and of a greyish metallic lustre on fracture. It had a sp. gr. 5, a hardness 8, was distinctly crystalline, and had a conchoidal fracture. It was weakly attacked by hot acids and was not altered by exposure to the air. Analyses of the product gave 82 per cent. of chromium, a result which indicates  $CrB$  as the probable formula of the compound.

*Tungsten Boride.*—As tungsten is closely related to chromium, it was selected as a promising element and a trial was made of its affinity for boron. The metal tungsten may be prepared from alkali tungstates by acidifying their solutions with hydrochloric acid. This causes the precipitation of the trioxide. After being dried, the trioxide can be reduced in the electric furnace, the charge used containing 10 parts of tungsten trioxide to one part of carbon.

For the preparation of the boride, 4 grams of tungsten were mixed with 0.2 gram of boron and then heated for 5 minutes by the aid of a current of 175 amperes and 65 volts. This produced a good fusion and the product was silvery and metallic on fracture. It was very brittle and under the microscope was seen to be crystallised in perfect octahedra. Its hardness was 8 and its sp. gr. 9.6. It was slowly attacked by concentrated acids, and vigorously by aqua regia. Analyses of the product showed the presence of 89 per cent. of metallic tungsten, a result which indicated the formula to be  $WB_2$ .

*Molybdenum Boride.*—The final compound prepared was a boride of molybdenum. This was selected, as the element molybdenum is closely related to chromium and tungsten and the metal is rather easily prepared.

The molybdenum was obtained by heating 300 grams of molybdenum trioxide and 30 grams of coke for 25 minutes with a current of 200 amperes and 65 volts.

For making the boride, 6 grams of metallic molybdenum were mixed with 1 gram of boron and heated for 20 minutes by the aid of a current of 230 amperes and 70 volts. This gave a homogeneous button with a

hardness of 9. It was quite brittle and on fracture showed a brilliant metallic lustre resembling that of pale brass. It was crystalline in structure, and its sp. gr. was 7.105. The substance was moderately attacked by hot concentrated acids and vigorously by hot aqua regia.

The formula  $\text{Mo}_3\text{B}_4$  was given to this compound as the result of several analyses which showed the presence of 86 per cent. of molybdenum.

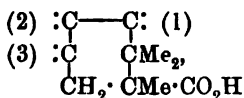
An attempt to make the borides of copper or bismuth failed entirely; in fact, there does not seem to be any affinity between boron and the members of the copper group.

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### III.—*The Constitution of the Acids obtained from $\alpha$ -Dibromocamphor.*

By ARTHUR LAPWORTH and WALTER H. LENTON.

WHEN  $\alpha$ -dibromocamphor is warmed with moist silver salts, it is in part transformed into the unsaturated monocyclic acid, bromocamphorenic acid (Trans., 1899, 75, 1134), in which, as has already been shown, the complex



must be assumed to be present, the ethylenic union existing between the atoms 1 and 2, or 2 and 3, to one of which also the bromine atom must be attached. The facts on which these statements were based are, briefly, as follows:—(1) the substance readily affords homocamphorenic acid on oxidation with mild oxidising agents (Trans., 1899, 75, 988), and (2) it is obtained from camphor, which contains the group  $\cdot\text{CMe}_2 \cdot \dot{\text{C}}\text{Me} \cdot \text{CO} \cdot$ , by a process which involves no violent action.

In the first paper, in which the constitution of bromocamphorenic acid was discussed, it was shown that when the acid is converted into  $\alpha$ -monobromocampholid, the lactonic oxygen atom becomes attached to the ring at the brominated carbon atom, the group  $\cdot\text{CBr} \cdot \text{OH} \cdot$  becoming

converted into  $\text{O} \begin{array}{c} \cdot\text{CBr} \cdot \text{CH}_2 \cdot \\ | \\ \text{O} \end{array}$ . This conclusion was confirmed later by the observation that camphonic acid, the acid which is formed on hydrolysing the lactone, contains the carbonyl group  $\cdot\text{CO} \cdot$  in the ring, indicating that the first stage in the hydrolysis is the formation of an acid in which the group  $\cdot\text{C}(\text{OH})\text{Br} \cdot$  is present.

Arguing from the behaviour of simpler lactones, it was presumed that a  $\gamma$ -lactone would be formed in preference to a  $\delta$ -lactone, the bromine atom would then be attached to the carbon atom labelled 1 or 3, and it is here that the first dubious point in the argument appears, for it is by no means always legitimate to apply generalisations based on the behaviour of open chain compounds to substances containing closed rings. For this reason, we have again taken up the investigation, with the object of ascertaining to which of the carbon atoms, 1, 2, or 3, the bromine atom is attached, for, in so doing, the constitution of the interesting series of compounds obtained from  $\alpha$ -dibromocamphor would be determined beyond question.

It may be worth while to point out that the view to which one of us had come respecting the position of the bromine atom in question led to conclusions which did not appear to be altogether satisfactory. Thus, assuming that the bromine atom was attached to the carbon atom in position (1), the behaviour of camphonic acid towards substituting agents was not easily explained (compare *Trans.*, 1900, 77, 451), whilst the supposition that it was associated with carbon atom (3) led to the view that both camphonic and camphononic acids must be represented by formulæ containing the grouping  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot$  (*Trans.*, 1899, 75, 1139), a conclusion which, although in excellent agreement with the properties of camphonic acid, is altogether unsatisfactory in regard to the other substance, which behaves exactly as would an acid

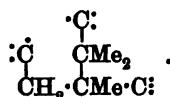
containing the complex  $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \cdot \text{C} \cdot \text{CO}$ , forming, for example, no additive compound at all with hydrogen cyanide (compare *Trans.*, 1901, 79, 379).

The first part of the investigation was therefore devoted to proving that, in the formation of camphonic acid from bromocamphorenic acid, no change of structure occurs, and that the ketonic oxygen atom occupies the position of the lactonic oxygen atom in the campholids. For this purpose, camphonic acid was reduced with sodium amalgam, and the product shown to be identical in all respects with the hydroxy-acid obtained by Forster on hydrolysing campholid itself (*Trans.*, 1896, 69, 57). The view already advanced of the mode of formation of camphonic acid seems, therefore, to be correct.

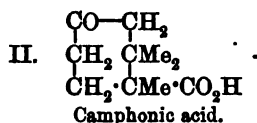
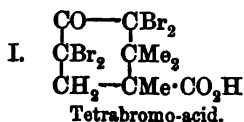
For the second part of the investigation, the tribromolactone obtained from camphonic acid (*Trans.*, 1900, 77, 458) was used as a starting point. This substance, being obtained by gentle treatment of camphonic acid with bromine, must be supposed to be derived from the tetrabromo-acid containing the group  $\cdot\text{CBr}_2\cdot\text{CO}\cdot\text{CBr}_2\cdot$ . It was hydrolysed by careful treatment with alkali, and the product, which we did not attempt to isolate, was oxidised by means of cold sodium hypo-

bromite, which was found to be the most suitable agent for the purpose. The oxidation product was isolated in the usual way and found to be a mixture, which, on further investigation, proved to contain trimethylsuccinic acid, a small quantity of camphoronic acid, and a relatively large amount of an acid,  $C_9H_{13}O_6$ , which proved to be the substance hitherto known as  $\beta$ -hydroxycamphoronic acid (Bredt, *Annalen*, 1898, 299, 158).

The formation of camphoronic acid from tribromocamphonolactone shows that the latter contains the complex

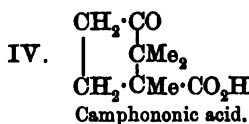
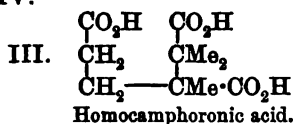


On inspecting the skeleton formula of camphorenic acid (p. 17) and remembering that the bromination of camphonic acid probably results in the first instance in the formation of a tetrabromo-acid containing the group  $\cdot\text{CBr}_2\cdot\text{CO}\cdot\text{CBr}_2\cdot$ , it will be seen that the only possible formula for this tetrabromo-acid is expressed by I, hence camphonic acid itself must have the constitution represented by II:



It follows of necessity, therefore, that in bromocamphorenic acid the bromine atom occupies the position of the ketonic oxygen in this formula, or in other words it is attached to the carbon atom 2 in the skeleton formula.

This, in itself, does not enable us to decide whether the double bond is situated between the atoms 1 and 2, or 2 and 3; the first alternative, however, is in all probability the correct one, for in this event homocamphoric acid and camphoronic acid will have the formulæ III and IV.

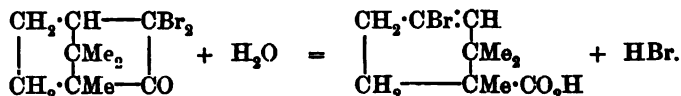


This conclusion is in complete agreement with the feeble ketonic properties of camphoronic acid, whilst the readiness with which camphonic acid forms additive compounds is explained by the presence in it of the complex  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot$ .

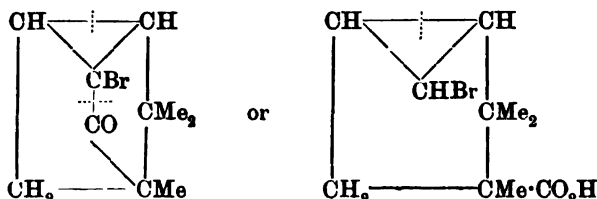
The conclusion thus arrived at harmonises with the whole of the known properties of the substances obtained by Forster (*Trans.*, 1896, 69, 36) and by Lapworth and Chapman (*Trans.*, 1899, 75, 986; 1900, 77, 446) and explains the apparent anomalies which have

appeared from time to time. The formula of camphononic acid, moreover, is what it should be on the basis of Bredt's formula for camphor and the relationship which has been firmly established between this acid and the simpler camphor derivatives (Trans., 1900, 77, 1056; 1901, 79, 1284).

The formation of bromocamphorenic acid from  $\alpha$ -dibromocamphor may be expressed by the scheme,



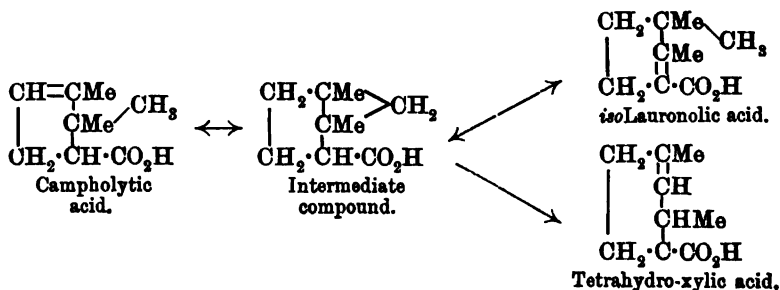
It is not impossible that at an intermediate stage a trimethylene ring is produced and that this afterwards breaks down, the carbon atom originally exterior to the ring having become merged in it. Thus intermediate compounds such as



might afford bromocamphorenic acid by scission at the points indicated by the dotted lines.

The ready formation of trimethylene rings in certain cases, notably in the production of carone and of the caronic acids (Perkin and Thorpe, Trans., 1899, 75, 522), makes it appear likely that the phenomenon is not so infrequent as is generally supposed.

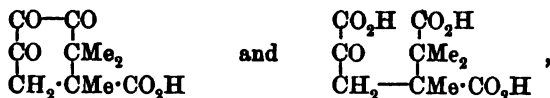
The assumption that an unstable trimethylene ring is formed in many other changes would probably be of great value in explaining their progress. Thus the curious transformations of campholytic and *isolauronolic* acids one into the other (Walker, Trans., 1900, 77, 378), and into derivatives of tetrahydro-xylic acid (Perkin and Lees, Trans., 1901, 79, 323), may be the result of reactions like the following :



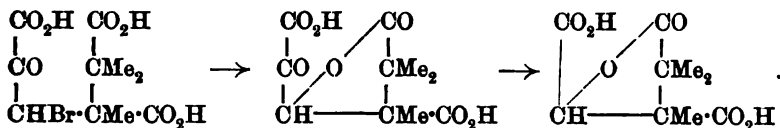
Similarly, the formation of camphene derivatives from bornyl chloride and the allied substances, may be the result of a similar participation of a methyl group in the formation of a trimethylene ring, and most of the apparently anomalous properties of these compounds point to such an explanation as being the correct one (compare Marsh, Proc., 1899, 15, 54).

As already mentioned, " $\beta$ -hydroxycamphoronic acid" is produced to a far greater extent than camphoronic acid in the oxidation of the product of hydrolysis of tribromocamphonolactone. It may appear at first sight to be somewhat remarkable that this should be the case, as it is impossible to suppose that the substance is obtained by the oxidation of camphoronic acid. If it be remembered, however, that the product of hydrolysis consists largely of ketonic substances, which are usually easily attacked by hypobromites, there is no great difficulty in explaining the formation of the "hydroxy"-compound.

Thus, for example, the product in the first instance may consist of a mixture of substances such as



and either of these might be attacked by the hypobromite, the latter, for example, affording successively the substances represented by the formulæ



The substance known as  $\beta$ -hydroxycamphoronic acid is, in reality, a lactonic acid containing water of crystallisation and should more correctly be termed  $\beta$ -camphoronic acid, employing the word used by Bredt for the isomeric substance. The hydrated acid,  $\text{C}_9\text{H}_{14}\text{O}_6 \cdot 2\text{H}_2\text{O}$ , is dibasic and may be boiled with excess of  $N/10$  alkali for half an hour without suffering any appreciable amount of hydrolysis into the hydroxy-acid. This fact rendered its identification a matter of considerable difficulty, for it is described as a tribasic acid both by Kachler and Spitzer and by Bredt. It was necessary, therefore, to prepare the acid directly from camphoronic acid, by the process which is described later, and it was then found that the conclusions which we had arrived at with regard to the acid from tribromocamphonolactone held good with regard to the other, the two substances being identical in every respect.



## EXPERIMENTAL.

*Reduction of Camphonic Acid.*

Camphonic acid, dissolved in 10 per cent. aqueous sodium hydroxide, was placed in an evaporating dish, carbon dioxide passed rapidly through the solution, and sodium amalgam added in small quantities during the course of several hours, until a small portion, after acidification with acetic acid, gave only a slight precipitate with *p*-bromophenylhydrazine acetate, indicating the absence of all but a trace of the ketonic acid. The liquid was separated from the mercury, acidified with dilute sulphuric acid and extracted repeatedly with ether; the ethereal solution was then washed with a very little water, dried, and evaporated. The colourless, oily residue slowly solidified to a mass of needles, which was crystallised from ethyl acetate. The hydroxy-acid finally formed large prisms, which melted and evolved gas at 178—179°. On analysis:

0.1236 gave 0.2902 CO<sub>2</sub> and 0.1073 H<sub>2</sub>O. C = 64.0; H = 9.6.

C<sub>10</sub>H<sub>18</sub>O<sub>8</sub> requires C = 64.5; H = 9.7 per cent.

The acid dissolved slowly in strong sulphuric acid, and on pouring the colourless solution into water a flocculent, white mass separated. This was collected, dried, and crystallised from light petroleum, from which it was deposited in fern-like, camphoraceous crystals melting at 177—178°; it had the properties of a lactone and was identical with the campholid obtained by the action of strong sulphuric acid on camphorenic acid (Forster, *Trans.*, 1896, 69, 56). The hydroxy-acid was identical with that which Forster obtained on hydrolysing the lactone (*loc. cit.*).

*Degradation of Camphonic Acid.*

Camphonic acid was first converted into tribromocamphonolactone by the method described in a former paper (*Trans.*, 1900, 77, 458), and the lactone carefully purified by crystallisation from chloroform.

The pure substance, which was in the form of large crystals, was finely powdered and covered with a 25 per cent. solution of potassium hydroxide containing some alcohol. No considerable rise of temperature occurred. The whole was allowed to remain for a week, then warmed on the water-bath for 15 minutes and poured into twice its bulk of water, the alcohol being got rid of by repeated evaporation with water nearly to dryness. The aqueous solution of the residue was then acidified, and extracted repeatedly with ether in the usual way. The ether, on evaporation, deposited an oily mass which slowly solidified. This was not closely examined, but was found to contain

only a trace of bromine ; it exhibited marked ketonic properties and its solution in alkalis had a distinct yellow colour.

The oil was dissolved in dilute sodium hydroxide, cooled to  $0^{\circ}$ , and to this solution sodium hypobromite solution was added, in small quantities at a time ; after each such addition, a notable rise in temperature occurred, and the process was continued until, after the lapse of 15 minutes, hypobromite could be detected in the liquid. Sodium sulphite was then added, the solution neutralised with hydrochloric acid and evaporated to a small bulk, a large excess of hydrochloric acid added, and the deposit of sodium chloride and bromide removed by filtration and thoroughly washed with ether. The filtrate was extracted twenty times with ether, and the ethereal solution dried and evaporated.

The oily residue thus obtained was dissolved in a little water, the solution made alkaline with baryta water, and the very slight deposit of insoluble matter removed. The filtrate was then heated to boiling, when a second and much larger deposition of insoluble substance occurred ; this was removed, washed with water, decomposed by means of hydrochloric acid, and the product examined.

The amount of acid obtained from the precipitate was too small for analysis as well as satisfactory examination. The substance was found to melt at  $137^{\circ}$  when very slowly heated, and at higher temperatures when the capillary tube was plunged into sulphuric acid already at that temperature. It formed an anilic acid melting at  $146^{\circ}$ , and a faintly alkaline solution of the ammonium salt gave no precipitate with barium or calcium chloride in the cold, but a copious one on boiling. In fact, the chemical and crystallographical properties of the acid were identical in every respect with those of camphoronic acid.

As it appeared, from the small quantity of camphoronic acid obtained, that this substance did not constitute the principal product of the oxidation, the acids in the filtrate from the barium camphoronate were liberated, extracted with ether, and, after the usual process of purification, were allowed to remain with a little water for several months. During this time, the mixture became semi-solid, and was at last spread on porous earthenware to drain. The solid portion was crystallised repeatedly from boiling water, when it was finally obtained in beautiful, lustrous prisms, which, after drying in the air for 2 days, did not lose their brilliancy, but on exposure at  $100^{\circ}$  rapidly became opaque and diminished in weight, owing to loss of water. On analysis:

0.1648 gave 0.3212  $\text{H}_2\text{O}$  and 0.0852  $\text{H}_2\text{O}$ .  $\text{C} = 49.8$  ;  $\text{H} = 5.7$ .

$\text{C}_9\text{H}_{12}\text{O}_6$  requires  $\text{C} = 50.0$  ;  $\text{H} = 5.6$  per cent.

The equivalent was determined by titration against  $N/10$  sodium

hydroxide in presence of phenolphthalein. The number found was 107, whereas a dibasic acid of the formula  $C_9H_{12}O_6$  requires 108.

The substance dissolved fairly readily in hot water, and in ethyl acetate, alcohol, or acetone, but only very sparingly in benzene, and was insoluble in light petroleum. It melted sharply at  $246^\circ$ .

The crystals from water were well-formed, rectangular plates or stout prisms, belonging apparently to the rhombic system; in the plates, the axial plane was parallel to the large face, and the direction of the acute bisectrix was at right angles to the direction of greatest length. The anhydrous substance, when melted on a glass slip beneath a cover-glass, solidified rapidly, forming radiate or fan-shaped structures split up by linear air-spaces.

The function of the third pair of oxygen atoms was not easy to determine, but as the substance gave no oxime, phenylhydrazone, or acetyl derivative, it was surmised that a lactone ring was present in the molecule. A small quantity of the acid was therefore heated to boiling with a known excess of  $N/10$  sodium hydroxide for half an hour, and, after cooling, the excess of alkali remaining was determined. It was found that no hydrolysis had occurred, the acid remaining dibasic, as before.

As the acid had a composition and a melting point identical with those of " $\beta$ -hydroxycamphoronic acid," obtained by Kachler and Spitzer from camphoronic acid, it was thought possible that the two substances might be identical, although " $\beta$ -hydroxycamphoronic acid" is stated to be tribasic.

To obtain further evidence on the point, the acid was converted into its ethyl ester by treatment with absolute alcohol and hydrogen chloride. The substance thus obtained crystallised from a mixture of ethyl acetate and light petroleum in thin, six-sided plates melting at  $161^\circ$ , which is exactly the melting point given by Kachler and Spitzer for the ester of their acid. The identification of the acid was completed by preparing " $\beta$ -hydroxycamphoronic acid" by the method described later.

In order to ascertain whether the oxidation of the hydrolytic product of tribromocamphonolactone had proceeded further than to  $\beta$ -camphoronic acid, the syrupy mother liquors were extracted from the porous plate by hot water, and subjected to distillation in a current of steam for several hours in order to separate the volatile acids. The aqueous distillate was then carefully neutralised with milk of lime, filtered, and evaporated nearly to dryness. A granular salt separated towards the end of this operation, and was collected and decomposed by hydrochloric acid, the acid being extracted with pure ether in the usual way. The residue obtained on evaporating the

ethereal solution was again converted into calcium salt, which was collected and decomposed once more.

The acid which was thus obtained melted at 150—151°, formed an anhydride which melted at 36—37°, and was identical with that prepared from the trimethylsuccinic acid obtained by fusing  $\alpha$ -camphoronic acid with potassium hydroxide.

It appears, therefore, that the product obtained from tribromocamphonolactone by the above process consists mainly of  $\beta$ -camphoronic acid with small quantities of camphoronic acid and trimethylsuccinic acid, and it is remarkable that no  $\alpha$ -camphoronic acid could be detected, although it is a substance which would probably be isolated easily from such a mixture.

#### *Bromination of Camphoronic Acid.*

The action of bromine on camphoronic acid takes place only under pressure in closed tubes at 140° or thereabouts, and bromo-acids are not obtained, as hydrogen bromide is at once eliminated, and a mixture of the lactones of  $\alpha$ - and  $\beta$ -hydroxycamphoronic acids is formed. Brecht (*Annalen*, 1898, 299, 158) did not succeed in brominating camphoronic acid or any of its derivatives under the ordinary pressure, but found it necessary to conduct the bromination in closed tubes and to employ the purified anhydro-chloride.

The authors have found that, as in so many other cases, the action of bromine on the mixture obtained by treating the acid with phosphorus pentabromide does not lead to satisfactory results, but that if phosphorus pentachloride is employed, an excellent yield of the monobrominated compounds can be obtained. The procedure was as follows.

Camphoronic acid was converted into the anhydro-acid by heating it in a flask at about 130—140° until water vapour ceased to be evolved. The cooled and powdered product was then carefully mixed with phosphorus pentachloride (1 mol.), heated on the water-bath for half an hour, and allowed to cool. Bromine (1½ mols.) was then added, the temperature gradually raised to 100° during about an hour, maintained at that point for about 6 hours, and the product then poured on to ice and allowed to stand overnight.

The granular product thus obtained consisted almost entirely of a mixture of the anhydro-chlorides of  $\alpha$ - and  $\beta$ -bromocamphoronic acids, and these may be converted into the bromo-acids by boiling with nearly anhydrous formic acid.

To obtain the  $\alpha$ - and  $\beta$ -camphoronic acids, the mixture of bromo-acids was boiled with water for several hours and the liquid then cooled, and rendered faintly alkaline with baryta water. The barium salt of  $\alpha$ -camphoronic acid separated almost at once as a fine, crystalline

powder, and the acid obtained from this was used for the preparation of trimethylsuccinic acid for purposes of identification.

The filtrate from the barium  $\alpha$ -camphoranate was acidified with hydrochloric acid, extracted with ether, and the  $\beta$ -camphoranic acid examined. It was found to be identical in every respect with the acid obtained by the former process.

A quantity of  $\beta$ -camphoranic acid prepared in this way was crystallised from water; the clear crystals were then allowed to dry in the air and at once analysed:

0.2921 gave 0.4612  $\text{CO}_2$  and 0.1622  $\text{H}_2\text{O}$ .  $\text{C} = 43.1$ ;  $\text{H} = 6.2$ .

$\text{C}_9\text{H}_{12}\text{O}_6 \cdot 2\text{H}_2\text{O}$  requires  $\text{C} = 42.8$ ;  $\text{H} = 6.3$  per cent.

The equivalent of the acid in the hydrated crystals was determined by titration with  $N/10$  sodium hydroxide, using phenolphthalein as indicator. The number obtained was 130, whilst that required for a dibasic acid of the formula  $\text{C}_9\text{H}_{12}\text{O}_6 \cdot 2\text{H}_2\text{O}$  is 126.

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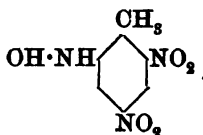
#### IV.—*Note on the Reduction of Trinitrobenzene and Trinitrotoluene with Hydrogen Sulphide.*

By JULIUS B. COHEN and HENRY D. DAKIN.

THE reduction of the 2:4:6-trinitrotoluene was originally undertaken with the object of producing an amino-group in the para-position, and by its removal of obtaining eventually 2:6-dinitrotoluene, a compound which we required in the study of the chlorination products of toluene.

The reduction of trinitrotoluene to 2:6-dinitro-4-toluidine by means of ammonium sulphide is described by Tiemann (*Ber.*, 1870, 3, 218) and Beilstein (*Ber.*, 1880, 13, 243), but the yield we obtained was small, and we did not succeed in improving it or in suppressing a quantity of tarry impurity which makes its appearance at the same time. After many unsuccessful attempts to effect reduction with ammonium sulphide and other agents, we tried a methyl alcoholic solution of crystallised ammonium sulphide, passing in hydrogen sulphide at the same time to displace air and keeping the whole well cooled. We found that the reaction proceeded vigorously even when the quantity of ammonium sulphide present was very far below the theoretical amount. Finally, we simplified the method by adding a few drops of concentrated ammonia to an alcoholic solution of the trinitro-

compound and saturating with hydrogen sulphide. The product, filtered from sulphur and poured into water, formed a bright yellow, crystalline precipitate, which was not the anticipated dinitrotoluidine, but, as we eventually discovered, 2:4-dinitro-6-tolylhydroxylamine,



Precisely the same reaction occurs with trinitrobenzene.

#### *2:4-Dinitro-6-tolylhydroxylamine.*

Twenty grams of finely powdered trinitrotoluene were suspended in about 100 c.c. of absolute alcohol, about 0.5 c.c. of concentrated ammonia was added, and the mixture cooled in ice. Hydrogen sulphide was then passed in with frequent shaking. In a short time, the colour of the solution deepened and the heavy crystals of trinitrotoluene, which at first settled to the bottom, were soon replaced by a thick, bulky, deep yellow precipitate, which filled the liquid. After about an hour, no further increase in the quantity of precipitate appeared, and the mixture was warmed for a moment on the water-bath and filtered quickly into a flask standing in ice. The precipitate was washed with hot alcohol until the filtrate was colourless. A residue of sulphur remained which weighed 6.3 grams. The alcoholic filtrate deposited, on standing, a mass of needle-shaped crystals, which were separated and amounted to 4.7 grams. This fraction contained a small proportion of dinitrotolylhydroxylamine, mixed with some compound of high melting point, and melted indefinitely from 130—160°. The product of high melting point is 2:6-dinitro-4-toluidine, for, on boiling 0.5 gram of this fraction for 2 hours with concentrated hydrochloric acid so as to convert the hydroxylamine compound into the insoluble 2:4-dinitro-6-toluidine, diluting and filtering, 0.3 gram of orange crystals melting at 167—169°, which is the melting point of the 2:6-dinitro-base, was deposited from the filtrate.

The filtrate was poured into water, which precipitated the bulk of the hydroxylamine compound. It was filtered, washed with water, and carefully dried. The weight was 11.5 grams. It was extracted with successive quantities of benzene, in which it all eventually dissolved, each portion being kept separate. The last extracts yielded crystals melting sharply at 143—145°, which did not change by successive recrystallisations and were therefore regarded as pure. The substance was analysed with the following results:

## 28 REDUCTION OF TRINITROBENZENE WITH HYDROGEN SULPHIDE.

0.2377 gave 39.5 c.c. moist nitrogen at 17° and 764 mm. N = 19.45.

0.1595 „ 27.25 „ „ 17° „ 760 mm. N = 19.79.

$C_7H_7O_5N_3$  requires N = 19.71 per cent.

A molecular weight determination by the boiling point method gave the following result :

0.181 gram in 11.43 grams of benzene raised the boiling point by 0.197°.

Mol. wt., found = 215 ; calculated = 213.

The compound reduces alcoholic silver nitrate, depositing a mirror ; it also reduces Fehling's solution. It readily dissolves in alcohol, but is less soluble in benzene and insoluble in light petroleum. From benzene, it crystallises in rhombohedra. It dissolves in boiling dilute hydrochloric acid unchanged and then crystallises in small, pale yellow needles. On prolonged boiling, it becomes insoluble and changes to a colourless, crystalline compound. The same result is much more rapidly effected by concentrated hydrochloric acid. Half a gram of the hydroxylamine compound, boiled with about ten times its weight of strong hydrochloric acid for half an hour, yielded 0.3 gram of the colourless substance.

### 2 : 4-Dinitro-6-toluidine.

The colourless compound was crystallised from benzene, from which it separated in needles melting at 212—213°. It was analysed with the following results :

0.1857 gave 0.2884  $CO_2$  and 0.0575  $H_2O$ . C = 42.35 ; H = 3.44.

0.1475 „ 27.7 c.c. moist nitrogen at 26° and 759 mm. N = 20.8.

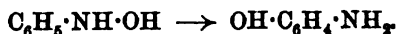
$C_7H_7O_4N_2$  requires C = 42.6 ; H = 3.5 ; N = 21.3 per cent.

0.220 gram in 8.1 grams of benzene raised the boiling point by 0.160°.

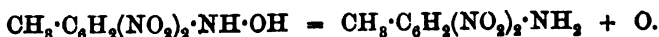
Mol. wt., found = 221 ; calculated = 197.

The substance is insoluble in sodium hydroxide solution or in dilute hydrochloric acid. Neither stannous chloride nor sodium nitrite in acid solution has any action on it. It dissolves unchanged in strong sulphuric acid and is reprecipitated by water.

The conversion of *p*-phenylhydroxylamine into *p*-aminophenol by mineral acids has been studied by Bamberger (*Ber.*, 1894, 27, 1349), and takes place by intramolecular rearrangement :



In the present case, the substance produced is not a phenol, but, according to analysis, a dinitrotoluidine. The conversion must therefore be accompanied by the removal of oxygen.



This is precisely what happens, for if the hydroxylamine compound be boiled with hydrochloric acid and indigo solution, the colour is slowly discharged, or with hydrochloric acid and potassium iodide, iodine is liberated.

As the amino-compound melts at  $212-213^{\circ}$ , it must be the 2:4-dinitro-6-toluidine, as the only other possible isomeride melts at  $166-168^{\circ}$ . This substance has not been previously prepared. As we have seen, the hydroxylamine compound acts both as a reducing and an oxidising agent. It is also worthy of remark that, whereas ammonium sulphide converts trinitrotoluene into 2:6-dinitro-4-toluidine, in which the *p*-nitro-group is reduced, the action of hydrogen sulphide is to reduce the nitro-group in the ortho-position.

### 1:3-Dinitro-5-phenylhydroxylamine.

This substance is prepared from 1:3:5-trinitrobenzene in exactly the same way as the tolyl derivative, but although the yield is smaller, the product is more readily obtained in a pure state. It forms dark orange crystals melting at  $114-116^{\circ}$ . Nine grams of trinitrobenzene yielded 4.5 grams of pure hydroxylamine derivative. Dinitrophenylhydroxylamine reduces alcoholic silver nitrate solution. On analysis, the following result was obtained :

0.113 gave 20.8 c.c. moist nitrogen at  $15^{\circ}$  and 756 mm.  $N = 21.53$ .  
 $C_6H_5O_5N_3$  requires  $N = 21.10$  per cent.

On boiling with concentrated hydrochloric acid, the substance at first passes into solution, but very soon a precipitate appears. The product is then poured into water, boiled up, and allowed to crystallise. On cooling, dark orange needles separate out, which melt sharply at  $158-159^{\circ}$ . This is the melting point of 3:5-dinitroaniline, with which it is undoubtedly identical, a fact which serves to confirm the nature of the reaction in the case of the tolyl derivative. We propose to continue this investigation.

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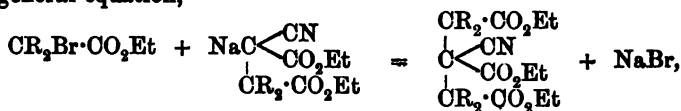
## V.—The Synthesis of Alkyltricarballic Acids.

By WILLIAM A. BONE and CHARLES H. G. SPRANKLING.

IN a previous communication (Trans., 1899, 75, 839), we described a method for the preparation of ethyl esters of cyanosuccinic acid and its alkyl derivatives; for some time past, we have been investigating a general method for the synthesis of alkyltricarballic acids, based

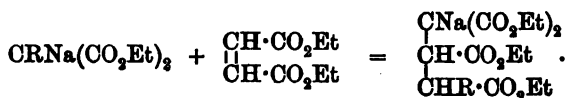


on the interaction of the sodium compounds of these ethyl cyano-succinates with the ethyl esters of  $\alpha$ -bromo-fatty acids, as indicated by the general equation,



where R indicates hydrogen or any alkyl radicle.

A reference to the literature of the subject shows that tricarballic acid and its  $\alpha$ -alkyl derivatives have been generally obtained by the condensation of the sodium compound of ethyl malonate, or one of its alkyl derivatives, with ethyl fumarate or maleate, and subsequent hydrolysis of the resulting ester, as follows :



Auwers and others (*Ber.*, 1891, 24, 307, 2887) prepared a number of  $\alpha$ -alkyltricarballic acids from ethyl fumarate, but so far as we know no attempt has been made to see whether dialkyltricarballic acids can be obtained by any similar method.

In 1896, Zelinsky (*Ber.*, 29, 333, 616) showed that three apparently stereoisomeric  $\alpha$ -dimethyltricarballic acids are obtained when the highest fraction of the oil which results from the interaction of ethyl cyanoacetate (1 mol.), sodium ethoxide (2 mols.), and ethyl  $\alpha$ -bromopropionate (2 mols.) in alcoholic solution is hydrolysed with sulphuric acid. His investigation of the subject was incomplete and he has since abandoned it.

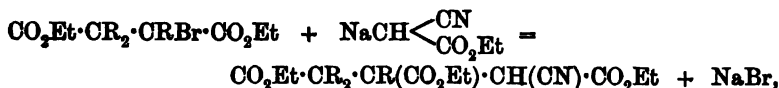
Just as we were beginning our experiments, Haller and Blanc (*Compt. rend.*, 1900, 131, 19) synthesised  $\alpha\alpha$ -dimethyltricarballic acid from ethyl cyanosuccinate, but except in this one instance the practicability of preparing tricarballic acids from ethyl alkylcyano-succinates has not so far been studied.\*

As the result of a long and systematic investigation of the matter, we have shown that any alkyltricarballic acid in which the alkyl radicle or radicles occupy an  $\alpha$ -position with respect to either of the two extreme carboxyl groups may readily be prepared by the method we have indicated.

Besides the method just discussed, there is obviously another possible way of passing over from an acid of the succinic to one of the tricarballic series, namely, by the interaction of an ethyl mono-

\* Since this paper was written, however, Dr. H. A. D. Jowett has published an account of the preparation of  $\alpha$ -ethyltricarballic acid from ethyl  $\alpha$ -cyano- $\beta$ -ethyl-succinate and ethyl bromoacetate (*Trans.* 1901, 79, 1846).

bromosuccinate with ethyl sodiocyanoacetate or malonate as represented by the general equation,



where R represents hydrogen or an alkyl radicle (or radicles). Hitherto, only tricarballic acid itself has been prepared by this method (Emery, *Ber.* 1890, 23, 3759), and we therefore extended our experiments in this direction in order to ascertain whether this second method possesses any advantages over the first, or *vice versa*. The results are very decisive on this point, for they indicate that whereas the first ("cyano-succinate") method is a general one, the second can only be applied in certain cases (owing partly to the circumstance that the bromination of many substituted succinic acids does not proceed regularly, and partly also to the tendency which some ethyl bromosuccinates exhibit to lose hydrogen bromide and form unsaturated compounds). And, further, even when the second method can be applied, the yields of resulting tricarballic acids are comparatively poor. Incidentally, however, we have accumulated valuable information as to the bromination of alkylsuccinic acids, which will be briefly discussed later.

During the course of the experiments, we have added to the knowledge of the properties of various alkyltricarballic acids, their anhydro-acids and monomethyl salts, but have not been able conjointly to finish the scheme of work originally drawn up; the results so far obtained are, however, sufficiently complete in themselves to justify their publication. The investigation of this interesting and important series of acids will be continued.

#### I. PREPARATION OF ETHYL CYANOTRICARBALLYLATES FROM ETHYL CYANOSUCCINATES.

The method adopted may be briefly described as follows: To a solution of 5.75 grams of sodium in alcohol is added one-fourth of a gram-mol. of the ethyl cyanosuccinate; the sodium compound of the latter, which is at once formed, remains in solution. Rather more than the calculated quantity of the  $\alpha$ -bromo-fatty ester is then cautiously added in small portions at a time. The interaction which follows is generally very vigorous, much heat is developed, and sodium bromide separates. The liquid usually becomes neutral after being heated for 30 to 60 minutes on the water-bath, after which it is poured into water and the ethyl cyanotricarballylate extracted with ether in the usual manner. On fractionating the crude oil under diminished pressure (20–35 mm.), a certain amount of it passes over at temperatures below 150°; the

thermometer then rises rapidly to about 200°, when the ethyl cyanotricarballylate begins to distil.

The following are the particulars concerning the yields, &c., obtained in the various preparations, and the properties of the refractionated ethyl cyanotricarballylates.

*Ethyl Cyanotricarballylate.*

The yield of refractionated oil obtained from ethyl cyanosuccinate and ethyl bromoacetate amounted to 75 per cent. of that theoretically possible; under 28 mm. pressure, it boiled at 206—212°. On being rapidly cooled, the distillate solidified. By dissolving the solid in the minimum quantity of warm glacial acetic acid, then adding hot water until a faint turbidity appeared, and setting the liquid aside to cool slowly, the whole of the substance separated after some hours in prismatic and transparent crystals which melted sharply at 40—41°. On analysis:

0.2213 gave 0.4421 CO<sub>2</sub> and 0.1376 H<sub>2</sub>O. C = 54.48; H = 6.90.

0.3116 „ 13.8 c.c. nitrogen at 18° and 752 mm. N = 5.07.

C<sub>13</sub>H<sub>19</sub>O<sub>6</sub>N requires C = 54.73; H = 6.66; N = 4.91 per cent.

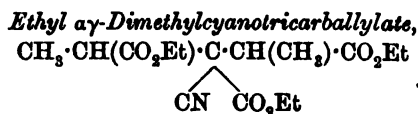


This substance may be prepared by the interaction of either the sodium derivative of ethyl β-methylcyanosuccinate and ethyl bromoacetate or of the sodium derivative of ethyl cyanosuccinate and ethyl α-bromopropionate. The first named method is much the better of the two, and the yield obtained by it amounted to 70 per cent. of the theoretical. The refractionated oil boiled at 202—204° under 23 mm. pressure, had a density  $d_{0^\circ/4^\circ} = 1.1329$ , and a refractive index  $\mu_{\text{Na}} = 1.4461$ . On analysis:

0.2002 gave 0.4137 CO<sub>2</sub> and 0.1316 H<sub>2</sub>O. C = 55.86; H = 7.31.

0.3102 „ 12.75 c.c. nitrogen at 15° and 771 mm. N = 4.87.

C<sub>14</sub>H<sub>21</sub>O<sub>6</sub>N requires C = 56.18; H = 7.02; N = 4.68 per cent.



The yield of refractionated oil obtained from ethyl β-methylcyanosuccinate and ethyl α-bromopropionate amounted to 65 per cent. of the theoretical. It boiled at 208—210° under 30 mm. pressure, had a

density  $d_{0^{\circ}/4^{\circ}} = 1.1215$ , and a refractive index  $\mu_{Na} = 1.4484$ . On analysis :

0.1976 gave 0.4146  $CO_2$  and 0.1353  $H_2O$ .  $C = 57.21$  ;  $H = 7.61$ .

0.2863 „ 11.3 c.c. nitrogen at  $16^{\circ}$  and 758 mm.  $N = 4.59$ .

$C_{15}H_{23}O_6N$  requires  $C = 57.50$  ;  $H = 7.34$  ;  $N = 4.47$  per cent.



This may be prepared either by the method adopted by Haller and Blanc (*loc. cit.*) by the interaction of ethyl sodiocyanosuccinate and ethyl  $\alpha$ -bromoisobutyrate, or by the interaction of ethyl  $\beta\beta$ -dimethylsodiumcyanosuccinate and ethyl bromoacetate. We have tried both methods and find that the second is by far the better one ; the yield obtained by it amounts to 55 per cent. of the theoretical, and if after fractionating the crude product the portion of lower boiling point be again heated with a small quantity of sodium ethoxide in alcohol, a further quantity of the cyanotricarballylate is formed, bringing the total yield up to nearly 70 per cent. of the theoretical.

The refractionated oil boiled at  $202-204^{\circ}$  under 17 mm. pressure, had a density  $d_{0^{\circ}/4^{\circ}} = 1.1353$ , and a refractive index  $\mu_{Na} = 1.4503$ . On analysis :

0.2006 gave 0.4206  $CO_2$  and 0.1341  $H_2O$ .  $C = 57.19$  ;  $H = 7.43$ .

$C_{15}H_{23}O_6N$  requires  $C = 57.50$  ;  $H = 7.34$  per cent.

*Ethyl  $\alpha\gamma$ -Diisopropylcyanotricarballylate.*

This was prepared by the interaction of ethyl  $\beta$ -isopropylsodiumcyanosuccinate and ethyl  $\alpha$ -bromoisovalerate ; the experiment cannot be properly carried out in an open vessel on the water-bath, as the reaction only proceeds very slowly under these conditions. The mixture was accordingly heated in soda-water bottles at  $100^{\circ}$  under pressure for 10—12 hours ; on fractionating the resulting crude oil under 15 mm. pressure, we obtained from 61 grams of ethyl  $\beta$ -isopropylcyanosuccinate originally taken the following fractions :

- |                                      |           |  |           |
|--------------------------------------|-----------|--|-----------|
| ( $\alpha$ ) Below $150^{\circ}$ ... | 33 grams. | ( $\gamma$ ) $205-215^{\circ}$ ...                   | 10 grams. |
| ( $\beta$ ) $150-205^{\circ}$ ...    | 37 grams. | ( $\delta$ ) Above $215^{\circ}$ , a few drops only. |           |

The fraction ( $\beta$ ) contained large quantities of nitrogen and bromine, and evidently consisted of a mixture of unchanged cyanosuccinate and bromoisovalerate ; the fraction ( $\alpha$ ) contained no nitrogen to speak of, but a large quantity of bromine. They were accordingly mixed, and after determining the amount of bromine in the mixture, the

corresponding quantity of sodium ethoxide in alcoholic solution was added to it. The whole was then heated in a soda-water bottle at  $100^{\circ}$  for 10 hours, as before, and on fractionating the resulting oil a further 10 grams passed over at  $205\text{--}215^{\circ}$  under 15 mm. pressure. This was mixed with the fraction  $\gamma$  obtained in the first part of the experiment, and the mixed oils were afterwards refractionated under 16 mm. pressure; finally, 17 grams of a nearly colourless oil boiling at  $208\text{--}212^{\circ}$  were obtained, which represent an 18 per cent. yield. On analysis:

0.2016 gave  $0.4672\text{ CO}_2$  and  $0.1596\text{ H}_2\text{O}$ .  $\text{C} = 63.2$ ;  $\text{H} = 8.8$ .

0.3259 „  $11.1\text{ c.c. nitrogen at } 5^{\circ}\text{ and } 762\text{ mm.}$   $\text{N} = 4.09$ .

$\text{C}_{10}\text{H}_{21}\text{O}_6\text{N}$  requires  $\text{C} = 63.51$ ;  $\text{H} = 8.65$ ;  $\text{N} = 3.90$  per cent.

The oil was very thick and viscous, it had a density  $d_{0^{\circ}/4^{\circ}} = 1.075$  and refractive index  $\mu_{\text{Na}} = 1.4595$ .

*Hydrolysis of the Oils.*—With the exception of ethyl  $\alpha$ -diisopropylcyanotricarballylate, all the oils just described can be readily hydrolysed by boiling them in a reflux apparatus for 10 to 20 hours with strong hydrochloric acid. This method we accordingly adopted. In no case did any solid acid separate on cooling the liquid after all the oil had dissolved, nor did we find it feasible to isolate the acids by means of their calcium salts, a plan which answers very well in the case of alkylsuccinic acids. We therefore resorted to the simple expedient of saturating the liquid in each case with ammonium sulphate and then thoroughly extracting it with pure ether. After drying the ethereal solution over anhydrous sodium sulphate and distilling off the solvent, there remained an oily residue which usually solidified in the course of a few hours. This was then either recrystallised from a suitable solvent, or, in cases where it consisted of a mixture of isomeric acids, was submitted to a suitable process for their separation. In one case, namely, that of  $\alpha\alpha$ -dimethyltricarballylic acid, the oil which remained after distilling off the ether did not solidify even after standing many days, and there was evidence that the hydrolysis had been incomplete; on heating the oil with dilute (10 per cent.) hydrochloric acid under pressure at  $190^{\circ}$  for a few hours, and afterwards evaporating the liquid in a vacuum over strong sulphuric acid, the pure acid was obtained.

## II. TRICARBALLYLIC ACIDS, THEIR ANHYDRO-ACIDS AND MONOMETHYL SALTS.

### *Tricarballylic Acid.*

The acid, after being recrystallised from a mixture of glacial acetic acid and chloroform, melted at  $157\text{--}159^{\circ}$ . On analysis:

0.1806 gave 0.2703  $\text{CO}_2$  and 0.0762  $\text{H}_2\text{O}$ .  $\text{C} = 40.81$ ;  $\text{H} = 4.69$ .

0.2164 silver salt gave 0.1407 Ag.  $\text{Ag} = 65.02$ .

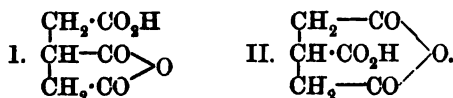
$\text{C}_6\text{H}_8\text{O}_6$  requires  $\text{C} = 40.90$ ;  $\text{H} = 4.54$  per cent.

$\text{C}_6\text{H}_8\text{O}_6\text{Ag}_3$  „  $\text{Ag} = 65.16$  per cent.

The dissociation constant of the acid is 0.022, a value practically identical with that given by Walker (0.0224) for tricarballic acid (Trans., 1892, 61, 707).

The calcium salts of this and the other acids of the tricarballic series described in this paper are readily soluble in cold water, but are almost entirely precipitated when the solution is boiled. When a 25 per cent. solution of calcium chloride is added to a cold solution of the neutral ammonium salt of tricarballic acid, no separation of the calcium salt occurs; on boiling the solution, however, a dense, crystalline precipitate instantly appears which entirely redissolves when the liquid is cooled again. The process of alternately precipitating and then redissolving the calcium salt may be repeated several times, but the precipitate seems very gradually to become less soluble in cold water. The behaviour of these calcium salts may be contrasted with those of the succinic acids which, when once precipitated from a hot solution of the ammonium salts, do not redissolve when the liquid is cooled. Acids of the two series may be readily separated by means of their calcium salts.

*Anhydro-acid.*—The characteristic property which the tricarballic acids possess of yielding anhydro-acids (generally crystalline) when they are boiled with acetyl chloride, or maintained at a temperature of  $200^\circ$  or upwards, was first noticed by Emery (*Ber.*, 1891, 24, 596) in the case of tricarballic acid itself. These anhydro-acids combine the functions of a true anhydride and a monobasic acid, but it has not yet been shown whether in their formation from the tricarballic acid, the elements of water are eliminated from the  $\alpha\beta$ - or the  $\alpha\gamma$ -carboxyl groups, or, in other words, whether, say in the case of tricarballic acid, the anhydro-acid has the formula I or II.



The best way of preparing these anhydro-acids is to dissolve the tricarballic acid in warm acetyl chloride, and, after boiling the solution for 2—3 hours in a reflux apparatus, to distil off the solvent and afterwards fractionate the residual liquid under diminished pressure. In the case of tricarballic acid, the anhydro-acid passed over between  $215^\circ$  and  $225^\circ$  under 45 mm. pressure; on cooling, it completely solidified, and after recrystallisation from a mixture of chloroform and glacial acetic acid, melted at  $130$ — $131^\circ$ .

0.1715 gave 0.2830  $\text{CO}_2$  and 0.0615  $\text{H}_2\text{O}$ .  $\text{C} = 45.10$ ;  $\text{H} = 3.98$ .

$\text{C}_6\text{H}_8\text{O}_5$  requires  $\text{C} = 45.57$ ;  $\text{H} = 3.79$  per cent.

The following investigation of the monomethyl salts of tricarballic acid shows that the anhydro-acid has probably the constitution expressed by the formula I.

*Monomethyl Salts.*—There are two possible isomeric monomethyl salts of tricarballic acid, and three methods by which they may be prepared, namely, (a) by the direct partial esterification of the acid; (b) by the partial hydrolysis of the trimethyl ester, and (c) by the solution of the anhydro-acid in methyl alcohol. We have carefully investigated these methods as follows.

(a) *Direct Esterification of the Acid.*—Five grams of the acid were heated for 10 minutes with methyl alcohol containing just sufficient dry hydrogen chloride to effect the esterification of one carboxyl group. The excess of alcohol was then distilled off under reduced pressure. A colourless oil\* remained, which entirely dissolved in a cold solution of sodium carbonate, and on being titrated with a standard solution of barium hydroxide proved to have an acidity corresponding to that of a methyl dihydrogen salt. The silver salt, prepared by adding silver nitrate to a solution of the oil exactly neutralised with dilute ammonia, was analysed as follows:

0.1726, on ignition, gave 0.0920 Ag.  $\text{Ag} = 53.30$ .

$\text{C}_7\text{H}_8\text{O}_6\text{Ag}_2$  requires  $\text{Ag} = 53.47$  per cent.†

There can be no doubt, therefore, that the oil had the composition of a methyl dihydrogen tricarballic acid. The next question to be decided was whether the oil was a single substance or a mixture of the two isomeric monomethyl salts. We accordingly determined its dissociation constant on the supposition that whereas a single monomethyl salt would give a value for the constant  $K$  which would remain practically the same for successive dilutions, a mixture of two isomeric monomethyl salts would be indicated by well-marked variations in the value of  $K$  on dilution. The results indicated that the oil was a single substance.

\* None of the methyl dihydrogen salts of tricarballic acids investigated by us are solids, so that it was impossible to purify them by crystallisation; nor did distillation under reduced pressure serve the purpose; the evidence of their purity is derived from a study of their dissociation constants.

† Besides analysing the silver salts of the monomethyl dihydrogen tricarballic acids described in the paper, we always ascertained the acidity of each by titration with a standard barium hydroxide solution. In each case, practically the calculated amount of the alkali was required.

*Dissociation Constant.*  $K = 0.0075$ . (Temp.  $25^{\circ}$ .)

$v$ .	$\mu_r$ .	$m$ .	$K$ .
7.62	8.27	0.0236	0.00748
15.24	11.65	0.0333	0.00753
30.48	16.42	0.0469	0.00756
60.96	23.03	0.0658	0.00761

(b) *Partial Hydrolysis of Trimethyl Tricarballoylate.*—It was first of all necessary to prepare the trimethyl ester from the acid by saturating a solution of it in methyl alcohol with dry hydrogen chloride in the usual manner. The resulting oil was washed with a dilute sodium carbonate solution, and distilled under 48 mm. pressure, when it passed over at  $205-208^{\circ}$ . It was then quite colourless, having a density  $d_{0^{\circ}/4^{\circ}} = 1.1381$ , and a refractive index  $\mu_{Na} = 1.4398$ . On analysis :

0.2110 gave 0.3823  $CO_2$  and 0.1246  $H_2O$ . C = 49.41 ; H = 6.56.

$C_9H_{14}O_6$  requires C = 49.50 ; H = 6.42 per cent.

Six grams of the oil were added to a quantity of potassium hydroxide, dissolved in methyl alcohol, just sufficient to effect the hydrolysis of two methoxy-groups. A drop of a methyl alcoholic solution of phenolphthalein was added, and the liquid allowed to stand at the ordinary temperature in an atmosphere free from carbon dioxide until only the faintest pink tinge remained. Two drops of a methyl alcoholic solution of methyl-orange were then added, and dry hydrogen chloride passed into the well-cooled liquid until a pink colour first appeared. The liquid was at once filtered from the potassium chloride which had separated, and the filtrate evaporated in an exhausted desiccator over sulphuric acid. The residual oil was dissolved in a slight excess of sodium carbonate solution, and the liquid extracted with pure ether in order to remove any trace of unchanged trimethyl ester. Finally, the solution was acidified with hydrochloric acid, and again extracted with pure ether. About 4.6 grams of a colourless oil were thus obtained ; the silver salt was prepared and analysed as follows :

0.2610 gave on ignition 0.1389 Ag. Ag = 53.32.

$C_7H_8O_6Ag_2$  requires Ag = 53.47 per cent.

Its dissociation constant was then determined as follows :

*Dissociation constant.*  $K = 0.00925$ . (Temp.  $25^{\circ}$ .)

$v$ .	$\mu_r$ .	$m$ .	$K$ .
11.47	9.15	0.0320	0.00922
22.94	15.78	0.0457	0.00926
45.88	22.12	0.0632	0.00929
91.76	30.94	0.0884	0.00933



These numbers show that the oil was a single monomethyl dihydrogen tricarballylate and isomeric with that obtained by the direct esterification of tricarballylic acid. Now it has been shown by V. Meyer, Sudborough, and other workers on the subject of esterification that a carboxyl attached to a primary carbon atom is much more easily esterified than one attached to a secondary carbon atom; consequently we must regard the monomethyl dihydrogen tricarballylate obtained by the direct esterification of the acid as the  $\alpha$ -compound,  $\text{CO}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and therefore the isomeric ester obtained by the partial hydrolysis of trimethyl tricarballylate must be the  $\beta$ -compound,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Me})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

(c) *By Solution of the Anhydro-acid in Methyl Alcohol*.—The anhydro-acid was boiled for 45 minutes in a reflux apparatus on a sand-bath with a quantity of pure dry methyl alcohol slightly in excess of that required to effect its conversion into the monomethyl dihydrogen salt. The liquid was then placed in a vacuum over sulphuric acid in order to get rid of the slight excess of alcohol, and, after some days, the residue was subjected to a further purification by means of sodium carbonate as described under (b). The silver salt of the purified oil was analysed as follows:

0.1167 gave on ignition 0.0611 Ag.  $\text{Ag} = 52.35$ .

$\text{C}_7\text{H}_8\text{O}_6\text{Ag}_2$  requires  $\text{Ag} = 52.47$  per cent.

The dissociation constant of the monomethyl salt was determined as follows:

*Dissociation constant.*  $K = 0.00945$ . (Temp.  $25^\circ$ .)

$v$ .	$\mu^\circ$ .	$m$ .	$K$ .
12.82	9.74	0.0342	0.00945
25.64	16.80	0.0480	0.00944
51.28	23.55	0.0673	0.00946
102.56	32.87	0.0939	0.00949

This shows, therefore, that the monomethyl dihydrogen tricarballylate obtained by dissolving the anhydro-acid in methyl alcohol is the  $\beta$ -compound,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Me})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and such as can only result from an anhydro-acid of the constitution represented by formula I (p. 35).

*$\alpha$ -Methyltricarballylic Acids*,  $\text{CH}_3\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

Since this acid contains two asymmetric carbon atoms, it exists in two inactive forms, meso- and racemic. Auwers, von Meyenberg, and Köbner (*Ber.*, 1891, 24, 307, 2887) succeeded in isolating these from the hydrolysed product of the condensation of ethyl fumarate

(1 mol.) with ethyl sodiomethylmalonate (2 mols). Their acids melted at  $134^{\circ}$  and  $184^{\circ}$  respectively, and it was shown that the isomeride of lower melting point is partially converted into the other on being boiled with strong hydrochloric acid.

Our experiments showed that when 26 grams of ethyl  $\alpha$ -methylcyanotricarballylate were hydrolysed with strong hydrochloric acid in the manner described, 16.5 grams of a mixture of isomeric acids were obtained; this only solidified after being kept for some days in ice. The substance, however, still contained a little nitrogen, and it was therefore heated with dilute (10 per cent.) hydrochloric acid in sealed tubes at  $180$ – $200^{\circ}$  for 24 hours. The solid which finally remained after evaporating the liquid to dryness melted between  $160^{\circ}$  and  $170^{\circ}$ . On rapidly extracting this residue with small quantities of cold water, one of the stereoisomeric acids dissolved, and the melting point of the residue gradually rose to  $179^{\circ}$  and afterwards remained constant. The washings, on evaporation, yielded a residue melting between  $136^{\circ}$  and  $145^{\circ}$ , and when this was once again subjected to fractional extraction with cold water, an acid melting at  $134$ – $135^{\circ}$  was obtained from the first washings.

The acids were analysed and their dissociation constants determined as follows:

*trans-Acid*, m. p.  $179^{\circ}$ .

0.1624 gave 0.2633  $\text{CO}_2$  and 0.0769  $\text{H}_2\text{O}$ . C = 44.11; H = 5.35.

0.3007 silver salt gave 0.1897 Ag. Ag = 63.10.

$\text{C}_7\text{H}_{10}\text{O}_6$  requires C = 44.21; H = 5.26 per cent.

$\text{C}_7\text{H}_7\text{O}_6\text{Ag}_3$  „ Ag = 63.39 per cent.

*Dissociation Constant.*  $K = 0.0322$ . (Temp.  $25^{\circ}$ .)

$v$ .	$\mu_{\infty}$	$m$ .	$K$ .
20.0	27.46	0.0767	0.0319
40.0	37.42	0.1069	0.0320
80.0	52.14	0.1489	0.0326
160.0	71.10	0.2032	0.0324

*cis-Acid*, m. p.  $134$ – $135^{\circ}$ .

0.2113 gave 0.3425  $\text{CO}_2$  and 0.1023  $\text{H}_2\text{O}$ . C = 44.09; H = 5.38.

$\text{C}_7\text{H}_{10}\text{O}_6$  requires C = 44.21; H = 5.26 per cent.

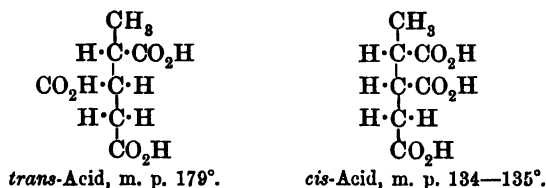
*Dissociation Constant.*  $K = 0.0480$ . (Temp.  $25^{\circ}$ .)

$v$ .	$\mu_{\infty}$	$m$ .	$K$ .
20.64	32.83	0.0938	0.0470
41.28	45.89	0.1311	0.0479
82.56	66.52	0.1900	0.0481
165.12	90.00	0.2583	0.0486

*Anhydro-acid.*\*—We have found that each acid on being dissolved in acetyl chloride yields its *own* liquid anhydro-acid, and that even after being distilled under reduced pressure neither of the anhydro-acids solidifies. Each anhydro-acid, however, with water yielded the acid from which it was originally derived, and on heating the *trans*-anhydro-acid with acetyl chloride, or acetic anhydride, for several hours, it was completely transformed into the *cis*-isomeride.

*Conversion of cis- into trans-Acid.*—We are able to confirm Auwers' observation that the *cis*-acid is partially converted into the *trans*-isomeride on being treated with hydrochloric acid under pressure at 190—200° and find that equilibrium is established when 80 per cent. is so transformed.

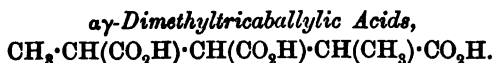
The behaviour of the anhydro-acids leaves no doubt as to the constitution of the two isomeric acids from which they are derived; the *cis*-anhydride is the more easily formed from its acid, and is more stable than the *trans*-isomeride. The two acids, therefore, have the following constitutions:



*Monomethyl Salts.*—So far we have only studied the monomethyl salts of the *cis*-acid; on determining the dissociation constants of those prepared by the three methods described in the case of tri-carballylic acid (pp. 36—38), we obtained practically identical numbers as follows:

Monomethyl salt prepared by	Mean values of <i>K</i> at 25°.
Direct esterification of acid .....	0·00893
Partial hydrolysis of trimethyl ester.....	0·00857
Solution of anhydro-acid in methyl alcohol .....	0·00888

At this stage of the inquiry we do not feel able to express any decided opinion as to the interpretation of these results, and the matter is receiving further investigation.



By the hydrolysis of the oil of higher boiling obtained by the interaction of sodium ethoxide (2 mols.) ethyl cyanoacetate, (1 mol.), and

\* Auwers did not study these substances.

ethyl  $\alpha$ -bromopropionate (2 mols.), Zelinsky (*loc. cit.*) obtained three isomeric acids,  $C_8H_{12}O_6$ , as follows :

	M. p. acid.	K for acid.	M. p. anhydro-acid.
(1)	203—204°	0.042	111—113°
(2)	175—176	0.054	129—130
(3)	148—149	0.051	117—119

and although his experiments were not quite conclusive, he brought forward evidence in favour of the view that the three acids are stereoisomeric  $\alpha\gamma$ -dimethyltricarballylic acids. If this be so, it is the only instance of the synthetical formation of three inactive stereoisomeric forms of a compound,  $C(abc)\cdot C(ab)\cdot C(abc)$ , corresponding to the three trihydroxyglutaric acids (the one *l*-avorotatory, to which there is, of course, a corresponding 'racemic' acid, and the other two 'meso'-inactive) obtained by Fischer (*Ber.*, 1891, **24**, 1842, 2686, 4222) by the oxidation of *l*-arabinose, xylose, and ribose respectively. The point seemed to us sufficiently important to warrant further and independent investigation. Briefly stated, our results are as follows.

When ethyl  $\alpha\gamma$ -dimethylcyanotricarballylate was hydrolysed by boiling it with excess of strong hydrochloric acid for 12 hours, and the resulting liquid extracted with ether, a solid mass was obtained which melted gradually between 140° and 160°. By boiling it for some time with successive small quantities of hydrochloric acid, part dissolved, leaving finally an insoluble constituent which melted at 206—207°, and was not altered by further treatment with hydrochloric acid. On concentrating the hydrochloric acid solution in a vacuum over sulphuric acid, two successive crops of crystals were obtained which melted at 170—188° and 171—173° respectively. This second fraction was twice recrystallised from strong hydrochloric acid and then melted sharply at 174°. We were unable to isolate any *third* acid either from the first crop of crystals melting at 170—188°, or from the hydrochloric acid mother liquors. The two acids melting at 206—207° and 174° were analysed, and their dissociation constants determined, as follows :

*Acid*, m. p. 206—207°.

0.1706 gave 0.2951  $CO_2$  and 0.0922  $H_2O$ .  $C = 47.19$  ;  $H = 6.01$ .

0.1064 silver salt gave 0.0654 Ag.  $Ag = 61.49$ .

$C_8H_{12}O_6$  requires  $C = 47.58$  ;  $H = 5.88$  per cent.

$C_8H_9O_6Ag_3$  „  $Ag = 61.70$  per cent.

*Dissociation constant.*  $K = 0.0445$ . (*Temp.* 25°.)

<i>v.</i>	$\mu_v$	<i>m.</i>	<i>K.</i>
33.71	40.18	0.1148	0.0441
67.42	55.81	0.1594	0.0448
134.84	75.93	0.2169	0.0446
269.68	101.70	0.2911	0.0443

*Acid*, *m. p.* 174°.

0.1926 gave 0.3302  $\text{CO}_2$  and 0.1038  $\text{H}_2\text{O}$ .  $\text{C} = 47.49$ ;  $\text{H} = 5.99$ .

0.1099 silver salt gave 0.0676  $\text{Ag}$ .  $\text{Ag} = 61.56$ .

$\text{C}_8\text{H}_{12}\text{O}_6$  requires  $\text{C} = 47.58$ ;  $\text{H} = 5.88$  per cent.

$\text{C}_8\text{H}_9\text{O}_6\text{Ag}_3$  „  $\text{Ag} = 61.70$  per cent.

*Dissociation constant.*  $K = 0.0545$ . (*Temp.* 25°.)

<i>v.</i>	$\mu_v$	<i>m.</i>	<i>K.</i>
20.7	35.03	0.1002	0.0559
41.4	48.67	0.1387	0.0540
82.8	66.72	0.1906	0.0542
165.6	90.60	0.2588	0.0546

*Anhydro-acids.*—Each acid dissolved in acetyl chloride, yielding its own solid anhydro-acid; that obtained from the acid of higher melting point (206—207°) fused at 110—112°, and that from the acid of lower melting point (174°) fused at 130°.

*Mutual Conversion.*—(1) The acid melting at 206—207° was heated for 4 hours at 180° under pressure with acetic anhydride, and from the dark-coloured liquid the acid melting at 174° was recovered by means of its potassium salt. It is clear, therefore, that the anhydro-acid of the former is at high temperatures converted into that of the latter.

(2) The acid melting at 174° was partially converted into that melting at 206—207° by heating it with strong hydrochloric acid at 210° for several hours.

There can be no doubt, therefore, that these two acids are identical with two of the acids obtained by Zelinsky, and, further, that they are stereoisomeric.

Zelinsky hydrolysed the oil from which he obtained his three acids with sulphuric acid; we therefore hydrolysed another portion of the ethyl  $\alpha$ -dimethylcyanotricarballylate by boiling it with 50 per cent. sulphuric acid. The operation was rather a slow one, and was only complete after 2 or 3 days. On cooling the liquid a crop of crystals, *A*, separated, melting at 190° or thereabouts; on further

concentrating the mother liquor, two more crops of crystals were obtained, namely, B, melting at 170—180°, and C, at temperatures below 139°. From fractions A and B, by further purification, were obtained two acids melting at 204—206° and 174—176°, identical in all respects with those obtained in the earlier experiments. Fraction C was submitted to two or three recrystallisations from water; its melting point gradually rose to 143° and then remained constant; analysis showed that it had the empirical formula  $C_8H_{13}O_6$ . On being treated with acetyl chloride, it yielded an anhydro-acid,  $C_8H_{10}O_5$ , melting quite sharply at 116—117°, which with water regenerated the original acid.

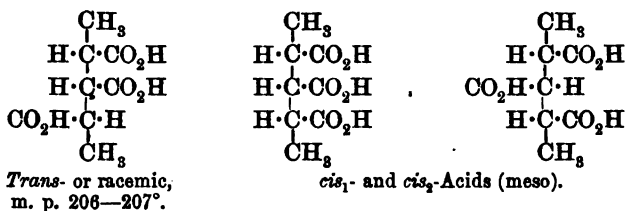
*Dissociation constant.*  $K = 0.0572$ . (Temp. 25°.)

<i>v.</i>	$\mu_r$	<i>m.</i>	<i>K.</i>
21.78	36.97	0.1056	0.0573
43.56	57.11	0.1460	0.0573
87.12	69.80	0.1994	0.0570
174.24	94.29	0.2693	0.0565

The most curious point about this acid is that on being warmed with strong hydrochloric acid it is very quickly and quantitatively transformed into the acid melting at 174°; for example, on recrystallising a portion of it from warm hydrochloric acid its melting point rose to 160—164°, after a second recrystallisation to 171—173°, and after a third to 174°.

The question therefore arises: Is this acid melting at 143° a third inactive stereoisomeric form of  $\alpha$ -dimethyltricarballic acid, or is it merely a molecular mixture of the other two forms? Three facts are in favour of the first view, namely (1) that it yields *its own* anhydro-acid with acetyl chloride; (2) that its dissociation constant varies very little with successive dilutions, and is higher than the corresponding values for the other two acids; and (3) that treatment with strong hydrochloric acid converts it into the second (174°) acid, whereas the acid melting at 206° remains absolutely unchanged when heated with hydrochloric acid under the ordinary pressure.

One of the three acids must be the racemic (*trans*-) form, the other two must be meso-modifications of  $\alpha$ -dimethyltricarballic acid which we may distinguish as the *cis*<sub>1</sub>- and *cis*<sub>2</sub>-acids. Since the anhydro-acid of the acid melting at 174° is the most stable of the three anhydro-acids at high temperatures, it is probably one of the *cis*- (meso-) forms; the other *cis*-form is, therefore, the acid melting at 143°. The someride having the highest melting point must therefore be the *trans*- or racemic form, as under:



At present we are unable to decide which of the two acids, melting at 174° and 143° respectively, is the *cis*<sub>1</sub>- and which the *cis*<sub>2</sub>-form. The further investigation of the subject is in hand, however.

*αα*-Dimethyltricarballic Acid,  $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{H}) \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

This acid is a very interesting member of the series, inasmuch as it is an oxidation product of pinonic acid (Tiemann and Semmler, *Ber.*, 1895, 28, 1349), also of fenchone (Gardner and Cockburn, *Trans.*, 1898, 63, 710) and camphoceanic acid (Jagelki, *Ber.*, 1899, 32, 1498). The acid we obtained by hydrolysing ethyl *αα*-dimethylcyanotricarballylate melted at 143°. On analysis:

0.2136 gave 0.3722 CO<sub>2</sub> and 0.1145 H<sub>2</sub>O. C = 47.51; H = 5.96.

C<sub>8</sub>H<sub>12</sub>O<sub>6</sub> requires C = 47.58; H = 5.88 per cent.

*Dissociation constant.*  $K = 0.0318$ . (*Temp.* 25°.)

<i>v.</i>	<i>μ<sub>s</sub>.</i>	<i>m.</i>	<i>K.</i>
23.67	29.16	0.0833	0.0320
47.34	40.39	0.1154	0.0318
94.68	54.67	0.1562	0.0315
189.36	75.12	0.2146	0.0309

The *anhydro-acid*, recrystallised from chloroform, melted at 135—136°. On analysis:

0.2022 gave 0.1900 CO<sub>2</sub> and 0.1003 H<sub>2</sub>O. C = 51.25; H = 5.50.

C<sub>8</sub>H<sub>10</sub>O<sub>5</sub> requires C = 51.61; H = 5.37 per cent.

The *trimethyl ester* was a thick oil boiling at 170—174° under 33 mm. pressure; it had a density  $d_{0^\circ/4^\circ} = 1.1403$  and a refractive index  $\mu_{Na} = 1.4417$ .

0.1829 gave 0.3588 CO<sub>2</sub> and 0.1236 H<sub>2</sub>O. C = 53.5; H = 7.51.

C<sub>11</sub>H<sub>18</sub>O<sub>6</sub> requires C = 53.7; H = 7.32 per cent.

*Monomethyl Salts.*—There are three possible isomeric monomethyl salts of this acid, namely, (a)  $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{H}) \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , (b)  $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{H}) \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , and (c)  $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{Me}) \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

We prepared monomethyl salts from the acid, the trimethyl ester, and the anhydro-acid, by the methods already described (pp. 36—38), with the following results :

(i) *By Direct Esterification of the Acid.*—A colourless oil.

0.1526 of its silver salt gave 0.076 Ag. Ag = 49.79.

$C_9H_{12}O_6Ag_2$  requires Ag = 50.00 per cent.

*Dissociation constant.*  $K = 0.0180$ . (Temp. 25°.)

<i>v.</i>	$\mu_{\nu}$	<i>m.</i>	<i>K.</i>
31.2	25.34	0.0724	0.0181
62.4	35.10	0.1003	0.0179
124.8	48.52	0.1386	0.0179
249.6	65.92	0.1883	0.0175

There can be no doubt, therefore, that the oil was a single substance, and from the fact that it was formed by the direct esterification of the acid (which contains only one primary  $CO_2H$  group), we may conclude that it has the formula (a).

(ii) *By Partial Hydrolysis of the Trimethyl Ester.*—A colourless oil.

0.2038 of its silver salt gave 0.1022 Ag. Ag = 50.12.

*Dissociation constant.*  $K = 0.00865$ . (Temp. 25°.)

<i>v.</i>	$\mu_{\nu}$	<i>m.</i>	<i>K.</i>
8.95	9.63	0.0275	0.00870
17.90	13.51	0.0386	0.00866
35.80	18.94	0.0541	0.00863
71.60	26.28	0.0751	0.00859

There can be no doubt that the oil was a single substance and quite different from that obtained by direct esterification of the acid, but we have no means of judging at present which of the two formulæ, (b) and (c), represents its constitution.

(iii) *From the Anhydro-acid.*—A colourless oil.

0.1286 of its silver salt gave 0.0642 Ag. Ag = 49.91 per cent.

*Dissociation constant.*  $K = 0.0186$ . (Temp. 25°.)

<i>v.</i>	$\mu_{\nu}$	<i>m.</i>	<i>K.</i>
12.52	15.89	0.0454	0.0189
25.04	23.14	0.0661	0.0186
50.08	31.96	0.0913	0.0183

This monomethyl salt, therefore, is probably the same as that obtained by the direct esterification of the acid. Comparing now the



values for  $K$ , determined for tricarballic and  $\alpha\alpha$ -dimethyltricarballic acids and their monomethyl salts,

	Acid.	Monomethyl salt from		
		Acid.	Trimethyl ester.	Anhydro-acid.
Tricarballic.....	0.022	0.0075	0.00925	0.00945
$\alpha\alpha$ -Dimethyltricarballic	0.032	0.0180	0.00865	0.01860

we see that in both cases the monomethyl salt obtained by the direct esterification of the acid is quite different from that obtained by the partial hydrolysis of the trimethyl ester; but that the salt obtained from the anhydro-acid is in the one case identical with that obtained from the trimethyl ester, and, in the other case, with that yielded by direct esterification of the acid.

#### *$\alpha\gamma$ -Diisopropyltricarballic Acids.*

These acids were prepared with the view of determining whether the substitution of two isopropyl groups in  $\alpha\gamma$ -positions has an influence upon the dissociation constant of tricarballic acid at all comparable with that exerted upon the constant of succinic acid by the symmetrical substitution of two hydrogen atoms by isopropyl groups (compare Trans., 1900, 77, 667).

*Ethyl  $\alpha\gamma$ -diisopropylcyanotricarballylate* is a difficult oil to hydrolyse; we found it best to perform the operation in two stages, namely, (1), with alcoholic potassium hydroxide, and (2), with 50 per cent. sulphuric acid. Finally, on extracting the acid liquid with ether we obtained from 17 grams of oil 9.8 grams of a solid mixture of stereoisomeric acids. These were difficult to separate, but on dissolving the mixture in water, saturating the solution with hydrogen chloride, and allowing it to stand for some time, we were able to resolve it into fractions of higher and lower melting point, by reason of the greater solubility of the latter. Two pure stereoisomeric acids were finally obtained, melting at  $173^\circ$  and  $156^\circ$  respectively. Each yielded its own liquid anhydro-acid, but we had not sufficient material to investigate these properly, and it is possible that, had we been able to purify them further they would have solidified.

The acid of higher melting point was transformed into the anhydro-acid of its isomeride on being boiled for many hours with acetyl chloride.

Each acid was analysed, and its dissociation constant determined as follows:

*Acid*, m. p.  $173^\circ$ .

0.2326 gave 0.4707  $\text{CO}_2$  and 0.1653  $\text{H}_2\text{O}$ .  $\text{C} = 55.18$ ;  $\text{H} = 7.90$ .

0.1687 silver salt gave 0.0943 Ag.  $\text{Ag} = 56.40$ .

$\text{C}_{12}\text{H}_{20}\text{O}_6$  requires  $\text{C} = 55.38$ ;  $\text{H} = 7.69$  per cent.

$\text{C}_{12}\text{H}_{17}\text{O}_6\text{Ag}_3$ ,  $\text{Ag} = 55.90$  per cent.

*Dissociation constant.*  $K = 0.193$ . (Temp. 25°.)

<i>v.</i>	$\mu_{\nu}$	<i>m.</i>	<i>K.</i>
171.5	151.6	0.4332	0.193
343.0	191.5	0.5469	0.192
686.0	233.1	0.6660	0.194
1372.0	270.7	0.7731	0.192

*Acid*, m. p. 156°.

0.1971 gave 0.3982 CO<sub>2</sub> and 0.1397 H<sub>2</sub>O. C = 55.09; H = 7.88.

0.2018 silver salt gave 0.1130 Ag. Ag = 55.99.

C<sub>12</sub>H<sub>20</sub>O<sub>6</sub> requires C = 55.38; H = 7.69 per cent.

C<sub>12</sub>H<sub>17</sub>O<sub>6</sub>Ag<sub>3</sub> „ Ag = 55.90 per cent.

*Dissociation constant.*  $K = 0.1625$ . (Temp. 25°.)

<i>v.</i>	$\mu_{\nu}$	<i>m.</i>	<i>K.</i>
95.9	113.7	0.3241	0.1621
191.8	148.8	0.4250	0.1628
383.6	188.3	0.5380	0.1633
767.2	230.0	0.6570	0.1640

If we compare these values with those for tricarballic acid (0.022) and  $\alpha$ -isopropyltricarballic acid (0.0434—Auwers, *loc. cit.*), we see at once that, in both cases, the introduction of the two isopropyl radicles has had a very marked 'raising' effect on the dissociation constant, but there is no such enormous difference between the constants of the two isomerides as there is between those of *cis*- and *trans*- $\alpha$ -diisopropylsuccinic acids.

The subject of the variation of dissociation constants with molecular constitution in this series of acids presents many interesting features, and will be discussed more fully in a future communication.

### III. TRICARBALLYLIC ACIDS FROM ETHYL BROMOSUCCINATES.

As already stated, we have studied the preparation of ethyl cyanotricarballylates by the interaction of ethyl bromosuccinates with the sodium compound of ethyl cyanoacetate, and have been able to carry it out in the following instances.

#### *Tricarballic Acid.*

The best method for preparing tolerably pure ethyl bromosuccinate, is to act on succinic anhydride with the calculated quantity of dry amorphous phosphorus and bromine, to form the dibromide of monobromosuccinic acid, and afterwards to pour the product into excess of

alcohol. In this way we obtained an 80 per cent. yield of ethyl bromosuccinate boiling at 140—143° under 29 mm. pressure. On condensing this with the calculated quantity of ethyl sodiocyanoacetate suspended in alcohol, a 70 per cent. yield of ethyl cyanotricarballylate resulted; when hydrolysed, this yielded tricarballylic acid, melting at 157—159°. On analysis:

0.2023 gave 0.3028 CO<sub>2</sub> and 0.0854 H<sub>2</sub>O. C = 40.81; H = 4.69.

C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> requires C = 40.90; H = 4.54 per cent.

*α-Methyltricarballylic Acid.*

On brominating 26 grams of monomethylsuccinic acid by the Hell-Volhard-Zelinsky method, pouring the product into alcohol, and extracting the resulting bromo-ester with ether, we obtained 38 grams of an oil which distilled over at 151—153° under 44 mm. pressure. On analysis:

0.4166 gave 0.2798 AgBr. Br = 29.07.

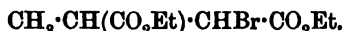
C<sub>9</sub>H<sub>15</sub>O<sub>4</sub>Br requires Br = 29.96 per cent.

There are two possible isomeric ethyl monobromomethylsuccinates, namely, (α) CH<sub>3</sub>·CBr(CO<sub>2</sub>Et)·CH<sub>2</sub>·CO<sub>2</sub>Et, and

(β) CH<sub>3</sub>·CH(CO<sub>2</sub>Et)·CHBr·CO<sub>2</sub>Et.

If the oil obtained by the method first indicated had the formula (α), then on condensing it with ethyl sodiocyanoacetate we should obtain the cyano-ester of β-methyltricarballylic acid; on the other hand, if it had the constitution (β), it would under similar treatment yield the cyano-esters of the α-methyltricarballylic acids.

On trying the experiment we obtained a 50 per cent. yield of an ethyl methylecyanotricarballylate (b. p. 235—245° under 30 mm. pressure) which, on hydrolysis with strong hydrochloric acid, yielded the two α-methyltricarballylic acids, melting at 177—180° and 134° respectively, but not a trace of any β-methyltricarballylic acid. Hence the ethyl monobromomethylsuccinate obtained when methylsuccinic acid is brominated in the manner described has the constitution



The two α-methyltricarballylic acids obtained were analysed as follows:

*Acid*, m. p. 177—180°.

0.1921 gave 0.3174 CO<sub>2</sub> and 0.0953 H<sub>2</sub>O. C = 44.0; H = 5.51.

0.3011 silver salt gave 0.1900 Ag. Ag = 63.10.

*Acid*, m. p. 134°.

0.2614 gave 0.4228 CO<sub>2</sub> and 0.1280 H<sub>2</sub>O. C = 44.11; H = 5.44.

0.1991 silver salt gave 0.1255 Ag. Ag = 63.06.

C<sub>7</sub>H<sub>10</sub>O<sub>6</sub> requires C = 44.21; H = 5.26 per cent.

C<sub>7</sub>H<sub>7</sub>O<sub>6</sub>Ag<sub>3</sub> „ Ag = 63.39 per cent.

*aa-Dimethyltricarballylic Acid.*

Twelve grams of *as*-dimethylsuccinic acid, on bromination by the Hell-Volhard-Zelinsky method, yielded 20 grams of monobromo-ester boiling at 159—164° under 70 mm. pressure. On analysis :

0.2442 gave 0.1589 AgBr. Br = 27.69.

$C_{10}H_{17}O_4Br$  requires Br = 28.47 per cent.

On condensing this with the calculated quantity of ethyl sodiocyanoacetate, we obtained a 50 per cent. yield of ethyl *aa*-dimethylcyanotricarballylate boiling at 210—220° under 35 mm. pressure. When hydrolysed with strong hydrochloric acid, this yielded *aa*-dimethyltricarballylic acid melting at 140—142°. On analysis :

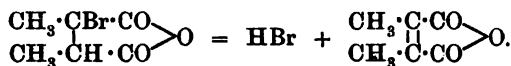
0.2611 gave 0.4554  $CO_2$  and 0.1408  $H_2O$ . C = 47.59 ; H = 5.99.

0.2122 silver salt gave 0.1308 Ag. Ag = 61.61.

$C_8H_{12}O_6$  requires C = 47.58 ; H = 5.88 per cent.

$C_8H_9O_6Ag_3$  „ Ag = 61.71 per cent.

We have also studied the bromination of *cis-s*-dimethylsuccinic acid by methods similar to those already described. Many workers have investigated the bromination of this and the isomeric *trans*-acid under varying conditions and with widely different results. Hell and Rothberg (*Ber.*, 1889, 22, 66) state that both acids behave normally on bromination, yielding *cis*-monobromodimethylsuccinic acid ; Zelinsky and Krapivin (*Ber.*, 1889, 22, 390), Bischoff and Voit (*Ber.*, 1890, 23, 390), and Auwers and Imhäuser (*Ber.*, 1891, 24, 2233), on the contrary, assert that neither acid can be brominated under any conditions, and that the substance which results is always the anhydride of pyrocinchonic acid (m. p. 95°), so that if any monobromo-anhydride (or acid) is momentarily produced it must at once lose hydrogen bromide as follows :



Our own experience shows that when a mixture of *cis-s*-dimethylsuccinic acid and amorphous phosphorus is treated with the quantity of dry bromine required to form the dibromide of the monobromo-acid, bromination certainly takes place, for on pouring the product into alcohol, and extracting and fractionating the resulting ester, we obtained a very fair yield of a bromo-ester containing 26.86 per cent. of bromine ( $C_{10}H_{17}O_4Br$  requires Br = 28.47 per cent.).

On condensing this bromo-ester with ethyl sodiocyanoacetate, sodium bromide was at once eliminated, but the product obtained was not a cyanotricarballylic ester, and up to the present we have not been

able to ascertain what really happened. The subject is still under investigation.

In conclusion, we wish to state that one of us is investigating the preparation and properties of tri- and tetra-methyltricarballic acids.

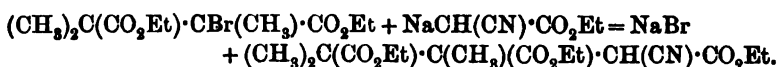
The cost of the materials required for this investigation has been largely defrayed out of grants from the Research Fund of the Society.

THE OWENS COLLEGE,  
MANCHESTER,

## VI.—*The Bromination of Trimethylsuccinic Acid and the Interaction of Ethyl Bromotrimethylsuccinate and Ethyl Sodiocyanoacetate.*

By WILLIAM A. BONE and CHARLES H. G. SPRANKLING.

IN connection with our investigations on the synthesis of alkyltricarballic acids, we have recently studied the bromination of trimethylsuccinic acid, and the interaction of ethyl bromotrimethylsuccinate and ethyl sodiocyanoacetate. Some years ago, one of us, in conjunction with Professor W. H. Perkin, jun., unsuccessfully attempted the synthesis of *i*-camphoronic ( $\alpha\alpha\beta$ -trimethyltricarballic) acid by a method involving this reaction, which is expressed by the following equation :



As a matter of fact, a crystalline acid melting at  $137^\circ$  and quite different from *i*-camphoronic acid was finally isolated from the hydrolytic products of the resulting cyano-ester, but the quantity obtained was too small to allow of a satisfactory investigation of its properties being made. The study of the subject was for the time being abandoned, partly on account of the difficulty experienced in preparing a sufficient quantity of trimethylsuccinic acid by any method then known, and also because Perkin and Thorpe succeeded in synthesising *i*-camphoronic acid by another method in 1897 (*Trans.*, 71, 1169). Since, however, the preparation of large quantities of pure trimethylsuccinic acid is no longer a difficult matter, we decided to reinvestigate the subject, and, if possible, to ascertain the cause of the earlier failure to synthesise camphoronic acid.

In 1898, Gustav Komppa (*Acta Soc. Scient. Fenn.*, 24, 1; also Abstr.,

1899, i, 419) tried to prepare bromotrimethylsuccinic acid by the action of phosphorus pentabromide on the corresponding hydroxy-acid. He was, however, unable to isolate any pure product from the complex mixture of substances obtained, and his experiments indicated that the three methyl groups in hydroxytrimethylsuccinic acid greatly hinder the replacement of hydroxyl by bromine.

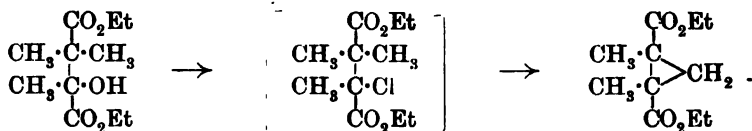
The results of our experiments may be briefly stated as follows :

(1) When trimethylsuccinic acid is heated with the calculated quantity of bromine under pressure at  $130^{\circ}$ , it is quantitatively converted into the characteristic white crystalline *bromotrimethylsuccinic anhydride* melting at  $197-198^{\circ}$ ; it is not possible to obtain the pure bromotrimethylsuccinic acid by dissolving this anhydride in hot water, since partial decomposition, with loss of hydrogen bromide, occurs during the process.

(2) If the bromination of trimethylsuccinic acid be carried out according to the Hell-Volhard-Zelinsky (phosphorus and bromine) method and the product poured into alcohol, a mixture of bromo-anhydride and ethyl bromotrimethylsuccinate results, from which it is very difficult to obtain the latter substance in a tolerably pure state.

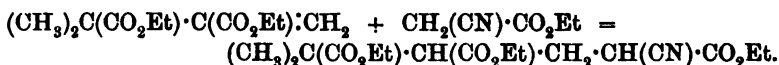
(3) Both the bromo-anhydride and ethyl bromotrimethylsuccinate readily lose hydrogen bromide under the influence of an alkali. By heating the bromo-anhydride with diethylaniline and subsequently pouring the liquid into a solution of potassium hydroxide, we obtained the potassium salt of *methylenedimethylsuccinic acid*,  $C_7H_{10}O_4$ . The ethyl ester of this acid very readily combines with hydrogen bromide, forming a bromo-ester,  $C_7H_{11}O_4Br$ , which, so far as we have been able to ascertain, seems to be identical with the ethyl bromotrimethylsuccinate,  $(CH_3)_2C(CO_2Et) \cdot CBr(CH_3) \cdot CO_2Et$ , prepared directly from trimethylsuccinic acid.

We would point out in this connection that Vincenzo Paolini (*Gazzetta*, 1900, 30, ii, 497), by acting on ethyl hydroxytrimethylsuccinate with phosphorus pentachloride, has obtained the ethyl ester of an acid,  $C_7H_{10}O_4$ , melting at  $153-154^{\circ}$ . Since this acid neither absorbed bromine or hydrogen bromide at the ordinary temperature, nor decolorised cold alkaline permanganate, he concluded that its molecule was not unsaturated, and described it as *dimethyltrimethylenedicarboxylic acid*. The formation of such an acid he explained by supposing that the ethyl chlorotrimethylsuccinate formed in the first instance by the action of phosphorus pentachloride on the ester of the hydroxy-acid at once loses hydrogen chloride, the elimination of which takes place between the chlorine and a hydrogen atom of a methyl group attached to the other carbon atom, so that 'ring-formation' occurs thus,

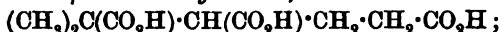


His acid certainly appears to have properties quite different from those of methylenedimethylsuccinic acid, and we are therefore led to the interesting conclusion that the elimination of hydrogen bromide from a bromotrimethylsuccinic derivative and of hydrogen chloride from a chlorotrimethylsuccinic molecule may occur in two entirely different ways. This is a point which certainly deserves further investigation.

(4) Ethyl bromotrimethylsuccinate reacts with ethyl sodiocyanoacetate, yielding the cyano-ester of a tribasic acid,  $\text{C}_9\text{H}_{14}\text{O}_6$ , melting at  $137\text{--}138^\circ$ , and isomeric with *i*-camphoronic acid (m. p.  $169\text{--}172^\circ$ ). The formation of such an acid can be explained on the supposition that ethyl bromotrimethylsuccinate loses hydrogen bromide, forming ethyl methylenedimethylsuccinate, which at once condenses with the ethyl cyanoacetate as follows :



If this interpretation of the matter be correct, the acid,  $\text{C}_9\text{H}_{14}\text{O}_6$ , obtained on hydrolysing the product with hydrochloric acid would be *aa*-dimethylbutane- $\alpha\beta\delta$ -tricarboxylic acid,



the results of a 'potash fusion' of the acid, which yielded acetic and trimethylsuccinic acids, are consistent with this view of its constitution.

#### EXPERIMENTAL.

##### *Bromination of Trimethylsuccinic Acid. Formation of Bromotrimethylsuccinic Anhydride and Ethyl Bromotrimethylsuccinate.*

(1) *Hell-Volhard-Zelinsky Method*.—We have at various times carried out experiments in which rather more than the calculated quantity of dry bromine was slowly dropped on a well cooled mixture of trimethylsuccinic acid and the theoretical amount of dry amorphous phosphorus. In each case, a vigorous reaction ensued accompanied by a strong evolution of hydrogen bromide, which only ceased after the mixture had been heated on the water-bath in a reflux apparatus for 6 or 8 hours.

On dropping the resulting brown liquid into an excess of alcohol (well cooled in ice) and afterwards pouring the alcoholic solution into a large excess of water, a heavy brown oil separated, which was

extracted with ether in the usual manner. After washing the ethereal solution with dilute (5 per cent.) sodium carbonate solution, then drying it over anhydrous sodium sulphate, and finally distilling off the ether, there remained a heavy reddish-brown oil which appeared to decompose when we tried to distil it under reduced pressure.

Analyses showed, however, that samples prepared at different times invariably contained from 30 to 33 per cent. of bromine, or considerably more than that required for ethyl bromotrimethylsuccinate,  $C_{11}H_{19}O_4Br$ , namely, 27.12 per cent.

*Bromotrimethylsuccinic Anhydride.*—After the oil had stood for some weeks in an exhausted desiccator over sulphuric acid, yellowish crystals began to separate; these were removed from time to time, and after being pressed on a porous plate were recrystallised from hot benzene. When quite pure, they melted sharply at 197–198°. The substance was insoluble in cold water or a cold solution of sodium carbonate, but readily dissolved in a warm solution of potassium hydroxide without, however, any formation of alcohol. It was, therefore, neither an acid nor an ester; the following analysis showed that it had a composition corresponding to that of bromotrimethylsuccinic anhydride, and a further study of its properties showed it to be this substance.\*

0.1691 gave 0.2368  $CO_2$  and 0.0600  $H_2O$ .  $C = 38.19$ ;  $H = 3.95$ .

0.2364 „ 0.2036  $AgBr$ .  $Br = 36.64$ .

$C_7H_9O_3Br$  requires  $C = 38.06$ ;  $H = 4.07$ ;  $Br = 36.20$  per cent.

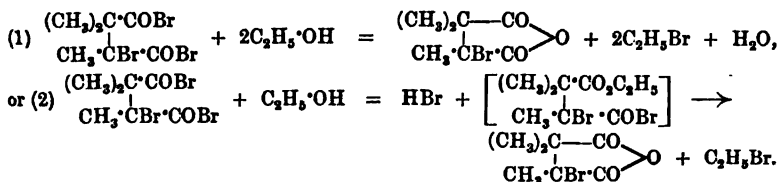
*Ethyl Bromotrimethylsuccinate.*—The crude oil was kept for several months until no further separation of bromoanhydride occurred: on analysing the residual oil, we obtained, for two different preparations, the following numbers:

(1) 0.5202 gave 0.3525  $AgBr$ .  $Br = 28.82$  per cent.

(2) 0.2528 „ 0.1713  $AgBr$ .  $Br = 28.83$  „

It, therefore, still contained 1.7 per cent. more bromine than that

\* Assuming that the dibromide of bromotrimethylsuccinic acid is produced by the action of phosphorus and bromine on trimethylsuccinic acid, the formation of this bromoanhydride can only be accounted for on the supposition that when the bromo-dibromide is dropped into alcohol, only part of it is decomposed, yielding ethyl bromotrimethylsuccinate, and that the other part reacts with the alcohol somewhat as follows:





required for ethyl bromotrimethylsuccinate, an indication that there remained a fair quantity of the bromo-anhydride in solution (a mixture of 81.3 parts of bromo-ester and 18.7 of bromo-anhydride would contain 28.8 per cent. of bromine). With a view to the complete esterification of this bromo-anhydride, the oil was repeatedly heated with an excess of ethyl alcohol containing 5 per cent. of hydrogen chloride ; by this means, the bromine was reduced to 28.0 per cent. As we subsequently found, however, that the bromo-anhydride, when treated with alcohol and hydrogen bromide, forms only the monoethyl salt, it was evident that the oil now consisted of a mixture of neutral and acid esters. We therefore dissolved it in pure ether and extracted the solution with a 5 per cent. sodium carbonate solution. On distilling off the ether, we found that the residual oil could now be fractionated under reduced pressure without undergoing any appreciable decomposition. Under 20 mm., the greater portion of it distilled over between 160° and 170° as a faint yellow oil having a very pungent odour. The following analysis indicated that it was practically pure ethyl bromotrimethylsuccinate :\*

0.2934 gave 0.1846 AgBr. Br = 26.76.

$C_{11}H_{19}O_4Br$  requires Br = 27.12 per cent.

(2) *Action of Bromine on Trimethylsuccinic Acid at 120—130°.*—Bromotrimethylsuccinic anhydride may be most conveniently prepared in quantity by the following method.

Five grams of trimethylsuccinic acid are heated with an equal weight of dry bromine in a sealed tube at 120—130° for 6 to 8 hours. The careful regulation of the temperature is important, since below 120° the bromination is not complete, and above 140° the contents of the tube are liable to char. Great care should be taken in opening such tubes after the heating, for the pressure in them is very great, and since dense clouds of hydrogen bromide are evolved it is advisable to carry out the operation in the open air. A solid with a slight orange colour remains after the pressure has been relieved ; sometimes it swells up considerably during the escape of gas, and may occasionally froth over out of the tube, and it is therefore advisable to have a large beaker at hand in which to receive any that may be so forced out. The solid should be washed with a cold dilute solution of sodium carbonate, dried on a porous plate, and recrystallised from hot benzene. The yield is quantitative.

\* The preparation of this ester is best carried out by dropping the brominated trimethylsuccinic acid into excess of ice-cold ethyl alcohol containing 5 per cent. of hydrogen bromide, heating the solution for about three hours on the water-bath to convert the bromo-anhydride into the monoethyl salt, and subsequently removing the latter by means of a cold 5 per cent. solution of sodium carbonate.

When pure, the bromo-anhydride melts at  $197-198^{\circ}$ ; it is quite insoluble in cold water or a cold dilute solution of sodium carbonate. We endeavoured to prepare bromotrimethylsuccinic acid by dissolving the anhydride in warm water and evaporating the solution until, on cooling, crystals appeared. In this way, colourless needles were obtained which, however, melted indefinitely between  $120^{\circ}$  and  $130^{\circ}$ , and contained only 31.1 per cent. of bromine; since the bromo-acid,  $C_7H_{11}O_4Br$ , requires 33.5 per cent. of bromine, it was evident that some decomposition had occurred during the solution of the bromo-anhydride, and a subsequent careful examination showed that hydrogen bromide is slowly liberated during the process.

*Action of Alcohol and Sodium Ethoxide on the Bromo-anhydride.*—On heating the bromo-anhydride with a molecular proportion of sodium ethoxide in ethyl alcohol, the liquid became neutral in about half an hour without, however, any separation of sodium bromide. On passing dry hydrogen chloride into the resulting liquid, sodium chloride separated, and as soon as the whole of the sodium had been thus eliminated the liquid was filtered and the clear filtrate evaporated in a vacuum over sulphuric acid. There finally remained a colourless, semi-solid mass containing 30.3 per cent. of bromine, which exhibited all the properties of an acid ester (ethyl hydrogen bromotrimethylsuccinate,  $C_9H_{15}O_4Br$ , requires  $Br = 30.0$  per cent.).

The same substance was obtained by heating the bromo-anhydride with an excess of ethyl alcohol in sealed tubes at  $160^{\circ}$  and afterwards distilling off the excess of alcohol on the water-bath. In neither of these experiments were we able to detect the formation of any neutral ester, and in each case the product instantly and completely dissolved in a cold solution of sodium carbonate with evolution of carbon dioxide. Our attempts to purify the substance by distillation under reduced pressure were unsuccessful, since decomposition began at temperatures below the boiling point.

We also made several unsuccessful attempts to prepare the silver salt of this acid ester, but as soon as silver nitrate was added to its aqueous solution neutralised with dilute ammonia, a copious yellow precipitate of silver bromide appeared, and we were not more successful in experiments in which freshly prepared silver carbonate was added to the aqueous solution.

*Action of Diethylaniline on the Bromo-anhydride. Methylenedimethylsuccinic Acid,  $C_7H_{10}O_4$ .*

As bromotrimethylsuccinic anhydride showed a tendency to lose hydrogen bromide on being boiled with water, we decided to study the action of diethylaniline on it with the view of preparing the corresponding unsaturated acid.

Accordingly, a solution of 10 grams of the bromo-anhydride in 15 grams of diethylaniline was heated in a reflux apparatus on a sand-bath for 10 hours, after which it was poured into a hot concentrated solution of potassium hydroxide. After the diethylaniline had been extracted with ether, the alkaline liquor was acidified, saturated with ammonium sulphate, and again extracted with ether. In this way a solid acid was obtained which was purified by dissolving it in excess of sodium carbonate solution, extracting resinous matter with chloroform, then boiling the solution with animal charcoal, finally acidifying and extracting it with pure ether. The pure acid was thus obtained as perfectly white crystals which melted at  $140-141^{\circ}$ . On analysis :

0.2063 gave 0.4010  $\text{CO}_2$  and 0.1290  $\text{H}_2\text{O}$ .  $\text{C} = 52.9$  ;  $\text{H} = 6.51$ .

$\text{C}_7\text{H}_{10}\text{O}_4$  requires  $\text{C} = 53.16$  ;  $\text{H} = 6.33$  per cent.

*Methylenedimethylsuccinic acid*,  $\begin{matrix} (\text{CH}_3)_2\text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{CH}_2 : \text{C} \cdot \text{CO}_2\text{H} \end{matrix}$ , melts at  $140-141^{\circ}$ , is fairly soluble in cold water, and, like other succinic acids, gives an insoluble calcium salt when a solution of its neutral ammonium salt is boiled with calcium chloride solution. Its aqueous solution instantly decolorises alkaline permanganate and rapidly absorbs bromine in the cold. The acid is readily esterified, and its liquid diethyl ester boils at  $173-176^{\circ}$  under 755—760 mm.

*Action of Bromine on the Diethyl Ester.*—On adding a solution of bromine in chloroform to the diethyl ester, the halogen at once disappeared ; as soon as no more of it was absorbed, the chloroform was distilled off and the residual oil at once hydrolysed with hydrochloric acid. On cooling, a white crystalline dibromo-acid separated, which after recrystallisation from hydrochloric acid melted at  $178-179^{\circ}$ . On analysis :

0.3027 gave 0.3529 AgBr.  $\text{Br} = 49.6$ .

$\text{C}_7\text{H}_{10}\text{O}_4\text{Br}_2$  requires  $\text{Br} = 50.0$  per cent.

*Action of Hydrogen Bromide on the Diethyl Ester.*—Ten grams of the diethyl ester were mixed with an aqueous solution of hydrogen bromide (saturated at  $0^{\circ}$ ). Much heat was evolved, the bromide being very quickly absorbed. The product was extracted with ether, and the ethereal solution washed with dilute sodium carbonate solution and afterwards dried over anhydrous sodium sulphate. On distilling off the ether there remained a liquid diethyl ester of a bromo-acid which contained an amount of bromine corresponding to that required for the empirical formula  $\text{C}_{11}\text{H}_{19}\text{O}_4\text{Br}$ . Thus :

0.4165 gave 0.2650 AgBr.  $\text{Br} = 27.07$ .

$\text{C}_{11}\text{H}_{19}\text{O}_4\text{Br}$  requires  $\text{Br} = 27.12$  per cent.

Most probably, therefore, this oil was ethyl bromotrimethylsuccinate,  $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)\cdot\text{C}(\text{CH}_3)\text{Br}\cdot\text{CO}_2\text{C}_2\text{H}_5$ , although it is just possible that it was the isomeric ethyl  $\alpha$ -methyl- $\delta$ -bromobutane- $\beta$ -dicarboxylate,  $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)\cdot\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)\cdot\text{CH}_2\text{Br}$ . On comparing the action of the oil with that of the ethyl bromotrimethylsuccinate obtained by the direct bromination of trimethylsuccinic acid (see p. 54) on ethyl sodiocyanoacetate (see next section), identical products were obtained in the two experiments. We afterwards found that the identity of these products does not necessarily imply the identity of the two bromo-esters in question, so that which of the two foregoing formulæ represents the constitution of the oil obtained by the action of hydrogen bromide on diethyl methylenedimethylsuccinate is a point we have not yet definitely established.

*Interaction of Ethyl Bromotrimethylsuccinate and Ethyl Sodiocyanacetate.*

(1) To a solution of 1.5 grams of sodium in 20 grams of alcohol were added 7.5 grams of ethyl cyanoacetate and 19 grams of ethyl bromotrimethylsuccinate; much heat was developed, sodium bromide separated, and the liquid became neutral after being heated for 3 hours on the water-bath. The product was extracted with ether and fractionated under 20 mm. pressure. A fair proportion of it passed over between  $130^\circ$  and  $150^\circ$ , the temperature then rose rapidly to above  $200^\circ$ , and about half of the oil distilled between  $210^\circ$  and  $215^\circ$ . This higher fraction was hydrolysed by boiling it with strong hydrochloric acid for 24 hours. On cooling the liquid, no crystals separated, so it was saturated with ammonium sulphate and thoroughly extracted with ether.

In this way, a white crystalline acid was isolated which, after recrystallisation from strong hydrochloric acid, melted sharply at  $137$ — $138^\circ$ . This, it will be observed, is the same melting point as that of the acid obtained by one of us and Professor Perkin some years ago by the same series of reactions. The acid was therefore not *i*-camphoronic acid (m. p.  $169$ — $172^\circ$ ), and, further, all attempts to isolate any camphoronic acid from the hydrolytic products by means of its characteristic barium salt entirely failed, so we can only conclude that none had been formed. Analysis of our acid, however, indicated that it was tribasic and isomeric with camphoronic acid,  $\text{C}_9\text{H}_{14}\text{O}_6$ , thus:

0.1364 gave 0.2500  $\text{CO}_2$  and 0.0813  $\text{H}_2\text{O}$ .  $\text{C} = 49.87$ ;  $\text{H} = 6.62$ .

0.1095 silver salt gave 0.0657 Ag.  $\text{Ag} = 60.0$ .

$\text{C}_9\text{H}_{14}\text{O}_6$  requires  $\text{C} = 49.53$ ;  $\text{H} = 6.42$  per cent.

$\text{C}_9\text{H}_{11}\text{O}_6\text{Ag}_3$  „  $\text{Ag} = 60.10$  per cent.

(2) In another experiment, 11 grams of the bromo-ester obtained by the action of hydrogen bromide on ethyl methylenedimethylsuccinate were added to the calculated quantity of ethyl sodiocyanoacetate suspended in alcohol. Sodium bromide at once separated and on continuing the experiment as described in the preceding paragraph, we finally obtained a cyano-ester boiling at 230—240° under 40 mm. pressure. This on hydrolysis with hydrochloric acid yielded the same acid,  $C_9H_{14}O_6$ , melting at 137°.

*Fusion of the Acid,  $C_9H_{14}O_6$ , with Potassium Hydroxide.*

In order to obtain evidence as to the constitution of the acid, 5 grams of the substance were fused with a paste of 30 grams of potassium hydroxide at 180—200°. A vigorous decomposition ensued. After being cooled, the fused product was dissolved in water, acidified with dilute sulphuric acid, and the liquid then distilled with steam. The distillate contained a fatty acid, the analysis of whose silver salt showed it was acetic acid.

0.2021 silver salt gave 0.1303 Ag.  $Ag = 64.47$ .

$C_9H_8O_2Ag$  requires  $Ag = 64.67$  per cent.

On extracting the residual liquor with ether, a solid acid melting at 147° and in other respects identical with trimethylsuccinic acid was obtained. (An analysis of the silver salt of this acid was made, but the results have, unfortunately, been mislaid; they agreed well with the calculated numbers for silver trimethylsuccinate.)

These results are quite consistent with the view that the acid  $C_9H_{14}O_6$  is *aa-dimethylbutane- $\alpha\beta$ -tricarboxylic acid*, and indeed it is difficult to see what other constitution could be assigned to it. The further investigation of its properties has, for the time being, been stopped on account of lack of material, but will be resumed in the near future.

We desire to state that the greater part of the materials required for this research was purchased out of a grant from the Research Fund of the Society.

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## VII.—*The Constituents of the Essential Oil of Asarum Canadense.*

By FREDERICK B. POWER and FREDERIC H. LEES.

THE aromatic essential oil distilled from the underground portion, rhizome, and rootlets of *Asarum canadense*, commonly known as Canada Snake-root, was first investigated by one of us a number of years ago (Power, *Inaug. Diss.*, Strassburg, 1880; *Proc. Amer. Pharm. Assoc.*, 1880, 28, 464). In that investigation, the following substances were isolated. (1) A terpene,  $C_{10}H_{16}$ , b. p.  $163-166^{\circ}$ ; (2) two fragrant alcohols, differing considerably in their boiling points and also in their odour, but both possessing the same empirical formula,  $C_{10}H_{18}O$ . The alcohol of lower boiling point,  $196-199^{\circ}$ , was termed *asarol*, and had an odour which recalled that of coriander, but was also somewhat camphoraceous, whilst the alcohol of higher boiling point,  $222-226^{\circ}$ , had a rose-like fragrance; (3) a fraction, possessing but little odour, b. p.  $254-257^{\circ}$ , representing the largest single constituent of the oil, which, upon oxidation with chromic acid, afforded an acid of the composition  $C_9H_{10}O_4$ . This acid was subsequently shown by Petersen (*Ber.*, 1888, 21, 1062) to be veratric acid and was obtained by him by the oxidation of an analogous substance contained in the oil of *Asarum europaeum*, boiling at about  $250^{\circ}$ , which he proved to be eugenol methyl ether; (4) a fraction collected at  $275-350^{\circ}$ , which contains a deep blue oil of undetermined composition; (5) a large amount of acetic acid, combined with the above-mentioned alcohols in the form of acetic esters, together with a very small amount of a less soluble, oily acid, which appeared to consist of, or at least to contain, valeric acid.

In consideration of the advance in knowledge of the constituents of essential oils since the period of the first investigation, and the means which are now available for the more positive identification and classification of these constituents by the preparation of well-defined and mostly crystallisable derivatives, it has seemed desirable again to subject the oil in question to a careful chemical examination.

### EXPERIMENTAL.

The oil employed for this research, about 2 kilos. in amount, was distilled by Messrs. Schimmel & Co. of Leipzig. Its density at  $15^{\circ}/15^{\circ}$  was 0.952, and its rotation  $\alpha_D = -3^{\circ}24'$  in a 100 mm. tube.

The oil was first shaken with a 5 per cent. solution of sodium carbonate in order to remove the free acids, which were examined in connection with the acids obtained by the subsequent hydrolysis of the

oil. It was then shaken three times successively with a 5 per cent. solution of sodium hydroxide, and afterwards with water until the washings were neutral. The combined alkaline liquids were shaken twice with ether to remove any adhering oil, then acidified with sulphuric acid, completely extracted with ether, and the ethereal liquid dried with calcium chloride. After distilling off the ether, the residual liquid was distilled in a vacuum. Under 10 mm. pressure, it began to distil at  $155^{\circ}$ , rising rapidly to  $250^{\circ}$ , and the last portion was observed to solidify in the condenser. When refractionated, there were obtained :

I. A light coloured oil boiling at  $172^{\circ}$  under 35 mm. pressure.

II. A dark oil which boiled somewhat below  $200^{\circ}$  under 10 mm. pressure and solidified on cooling.

*The Phenol,  $C_9H_{12}O_2$ .*

The first of the preceding fractions was distilled under the ordinary (762 mm.) pressure and afforded :

(1) A light greenish liquid, becoming brown on standing, and boiling below  $245^{\circ}$ .

(2) A light yellow liquid, boiling at  $245-260^{\circ}$ , which did not solidify at  $-16^{\circ}$ .

(3) A small residue, from which a little crystalline substance separated on cooling.

Of these fractions, (1) and (2) were analysed.

(1) 0.1402 gave 0.3606  $CO_2$  and 0.1008  $H_2O$ .  $C = 70.1$  ;  $H = 8.0$ .

(2) 0.1493 „ 0.3922  $CO_2$  „ 0.1066  $H_2O$ .  $C = 71.6$  ;  $H = 7.9$ .

These two fractions were then subjected to a final fractionation under the ordinary pressure, with the following result :

(a) A few drops only distilled below  $220^{\circ}$ .

(b) From  $220^{\circ}$  the mercury rose rapidly to  $245^{\circ}$ .

(c) The chief portion distilled between  $245^{\circ}$  and  $255^{\circ}$ , and was fairly constant at  $248-252^{\circ}$ .

(d) Only a few drops distilled above  $255^{\circ}$ .

Fraction (c) was then analysed.

0.1523 gave 0.3992  $CO_2$  and 0.1073  $H_2O$ .  $C = 71.5$  ;  $H = 7.8$ .

$C_9H_{12}O_2$  requires  $C = 71.1$  ;  $H = 7.9$  per cent.

These results indicate that the phenol contained in asarum oil has the empirical formula  $C_9H_{12}O_2$ . It is a nearly colourless, oily liquid, having an odour recalling, but more agreeable than, that of creosote. In the process of liberating the phenol from its alkaline solution a somewhat clove-like odour was developed, and this at first led us to suspect that the phenol contained some eugenol. This, however, is

rendered highly improbable, both on account of the constancy of the analytical results and the characteristic colour reaction which was afforded by all the fractions, but most strikingly by the principal fraction (c). Thus a very small quantity of the phenol, when dissolved in 90 per cent. alcohol, gives, with a trace of very dilute ferric chloride, a beautiful violet colour which only gradually fades, whilst eugenol, under the same conditions, gives a green. If, however, the phenol from asarum oil be dissolved in absolute alcohol, and a trace of a stronger solution of ferric chloride added, it affords a green colour, whilst eugenol, under these conditions, gives a deep blue. The amount of the phenol available did not permit of the formation of any derivatives, but as it is not identical with any of the known phenols of the formula indicated, it is evidently a new substance, and we shall endeavour to determine its constitution by some synthetical experiments.

#### *Identification of Palmitic Acid.*

It was noted that in the first distillation of the phenol, a solid substance separated in the condenser, and that in a subsequent fractionation the higher fraction, designated as II (p. 60), solidified on cooling. This was, therefore, brought upon a porous tile, and the substance subsequently dissolved in hot light petroleum, from which, on cooling it crystallised in colourless, pearly plates. Its melting point was 60—61°, and this remained unchanged on recrystallisation. On analysis, it was identified as palmitic acid :

0.0874 gave 0.2382 CO<sub>2</sub> and 0.0982 H<sub>2</sub>O. C = 74.3 ; H = 12.5.

C<sub>16</sub>H<sub>32</sub>O<sub>2</sub> requires C = 75.0 ; H = 12.5 per cent.

#### *Identification of Pinene.*

*Separation of the Terpene.*—The oil, which had been shaken with a dilute solution of sodium hydroxide as previously described, was washed with small, successive portions of water until the washings were neutral, and dried with anhydrous sodium sulphate. It was then distilled under diminished pressure and the portion collected which boiled below 100° under 10 mm. pressure. After several fractionations of this portion and drying with potassium carbonate, the lowest fraction, which distilled below 85° under 10—15 mm. pressure, was collected. Its density was 0.8566 at 18°/16°, which proved the absence of any olefinic terpene. These liquids were then further fractionated under the ordinary pressure, when the greater portion finally distilled below 165°, (α), chiefly at 159—161°, and only exceedingly small fractions were collected between 165° and 170° (β) and from 170—180° (γ). These were analysed, with the following results :



( $\alpha$ ) 0.1252 gave 0.4003  $\text{CO}_2$  and 0.1320  $\text{H}_2\text{O}$ . C = 87.2; H = 11.7.

( $\beta$ ) 0.1526 „ 0.4873  $\text{CO}_2$  „ 0.1606  $\text{H}_2\text{O}$ . C = 87.1; H = 11.7.

( $\gamma$ ) 0.1558 „ 0.4920  $\text{CO}_2$  „ 0.1628  $\text{H}_2\text{O}$ . C = 86.1; H = 11.6.

$\text{C}_{10}\text{H}_{16}$  requires C = 88.2; H = 11.8 per cent.

*Fraction below 165°*.—This fraction, boiling chiefly between 159° and 161°, which is seen to consist of a nearly pure hydrocarbon, amounted to about 2 per cent. of the original oil. Its physical constants were as follows:  $d_{16^\circ/16^\circ} = 0.8563$ .  $\alpha_D^{20} = +1.36'$ . It readily formed a crystallisable nitrochloride melting sharply at 103—104°. From the latter, the nitrolpiperidide was prepared, which, after recrystallisation from methyl alcohol, melted sharply at 118—119°. This fraction thus consisted of *pinene*, and its low rotation indicates it to be a mixture of the *d*- and *l*-forms. Petersen (*Ber.*, 1888, 21, 1059) has previously recognised the terpene existing in the oil of both the European and American species of *Asarum* as pinene, in the former as the *l*-variety, but identified it only by the formation of an oily monobromide and by its conversion into dipentene.

As it was possible that the very small fraction of our oil collected between 170° and 180° might contain dipentene or limonene, it was treated with bromine, but only an uncrystallisable, oily product was obtained. After being carefully dried, a bromine determination was made of this, with the following result:

0.2915 gave 0.3762 AgBr. Br = 54.9.

$\text{C}_{10}\text{H}_{16}\text{Br}_2$  requires Br = 54.1 per cent.

This result serves to prove the absence of either dipentene or limonene, both of which form crystallisable tetrabromides,  $\text{C}_{10}\text{H}_{16}\text{Br}_4$ . By a careful examination of all the fractions, no terpene other than pinene could be detected in the oil.

### *Hydrolysis of the Oil.*

For further examination, all the oil boiling above the terpene fraction was now hydrolysed by boiling with alcoholic potassium hydroxide for about 2 hours in a flask provided with a reflux condenser. After distilling off the greater portion of the alcohol from a water-bath, the liquid was brought into a separating funnel and sufficient water added to effect the separation of the oil. The latter was then drawn off, the aqueous alkaline liquid shaken with successive portions of ether, and the ether extracts mixed with the separated oil. The latter was then washed several times with water, and these washings added to the aqueous alkaline liquid. The ethereal solution of the oil was quickly dried with calcium chloride, filtered, the ether distilled off, and the residue finally subjected to fractional distillation, first

under diminished pressure, and then in part under the ordinary pressure. The following fractions were eventually obtained: 195—203°, 203—208°, 208—216°, 216—222°, 222—235°, 235—245°, and 245—260°.

### Identification of Linalool.

**Fraction 195—203°.**—This was a large fraction which, when re-distilled under the ordinary pressure, passed over mainly at 199° and almost entirely at 198—202° under 768 mm. pressure. It is a colourless, fragrant liquid. It was analysed and its physical constants were determined with the following results:

0.1372 gave 0.3910 CO<sub>2</sub> and 0.1436 H<sub>2</sub>O. C = 77.7; H = 11.6.

C<sub>10</sub>H<sub>18</sub>O requires C = 77.9; H = 11.7 per cent.

$d_{15.5^\circ/15^\circ} = 0.8711$ .  $\alpha_D = +10.48'$  in a 100 mm. tube;  $[\alpha]_D = +12.4^\circ$ .

When oxidised with chromic acid, it afforded citral, which was obtained as a pale yellow liquid of strong, lemon-like odour, distilling at 110—115° under a pressure of 10—12 mm. The latter, by condensation with pyruvic acid and  $\beta$ -naphthylamine, was converted into the crystalline  $\alpha$ -citryl- $\beta$ -naphthacinchonic acid, melting at 195—198°.

The identity of this fraction with d-linalool is therefore definitely established. It corresponds to the substance C<sub>10</sub>H<sub>18</sub>O (b. p. 196—199°), which in the first investigation of the oil was designated *asarol*.

**Fraction 203—208°.**—This fraction was too small for further examination, and evidently consisted simply of a mixture of the preceding and the following fractions.

**Fraction 208—216°.**—This was a small fraction, which distilled mostly between 208° and 212°. It was analysed, and its physical constants were determined, with the following results:

0.1368 gave 0.3866 CO<sub>2</sub> and 0.1424 H<sub>2</sub>O. C = 77.1; H = 11.6.

0.1472 „ 0.4154 CO<sub>2</sub> „ 0.1524 H<sub>2</sub>O. C = 77.0; H = 11.5.

C<sub>10</sub>H<sub>18</sub>O requires C = 77.9; H = 11.7 per cent.

$d_{15.5^\circ/15^\circ} = 0.911$ ;  $\alpha_D = -0.24'$  in a 100 mm. tube.

### Identification of Borneol.

The liquid had a camphoraceous and also somewhat rose-like odour. When subjected to a temperature of -10° for an hour, no crystalline substance separated. As this fraction of the oil was relatively small, and as its constituents were evidently contained to some extent in the next higher fraction, the two fractions were mixed. A portion, however, of the higher fraction was reserved for special examination.

This mixture of the two fractions was now gently oxidised with Fittig's oxidation mixture (*Ber.*, 1885, 18, 3207) in the following

proportions: 10 parts of oil, 80 parts of potassium dichromate, and 120 parts of sulphuric acid, the latter diluted with three times its volume of water. The oxidising mixture was added in small amounts at a time to the oil, which was kept cool by immersion of the containing flask in water. After all the chromic acid solution had been added, the mixture was heated on a water-bath for about 20—30 minutes. It was then distilled from a water-bath under diminished pressure and the camphor which separated in the condenser and distillate was collected by filtration, and dried on a porous tile. A little of the sublimed product was found to melt sharply at  $175^{\circ}$ . A determination of its specific rotation in 90 per cent. alcohol gave the following result:

$$\alpha_D = -1^{\circ}45'; l = 0.5 \text{ dcm.}; c = 8.684; [\alpha]_D = -40.3^{\circ}.$$

For further identification of the camphor, the oxime was prepared, and found to melt at  $115$ — $116^{\circ}$ . As camphor could not be detected in the fraction of the original oil, its formation by the above method of oxidation is conclusive proof of the presence of *l-borneol* in the oil.

The chromic acid liquor remaining from the distillation of the camphor was subsequently shaken out several times with ether, the ethereal solution washed with a little water, dried with calcium chloride, and the ether removed by distillation. The residual light yellow oil, which had a strong odour of acetic acid, was found to be not entirely soluble in cold sodium carbonate solution. It was consequently redissolved in ether and the ethereal solution shaken out several times with a dilute solution of sodium carbonate in order to remove the acids. The ethereal solution was then washed with a little water, dried with calcium chloride, and the ether removed by distillation. The residue was a light yellow oil possessing a coumarin-like odour, and on standing a short time became a crystalline paste. This was drained on a porous tile, when the substance was obtained quite white. After recrystallisation from dry ether it melted at  $62^{\circ}$ , and was insoluble in sodium carbonate solution. On analysis:

0.1148 gave 0.2731  $\text{CO}_2$  and 0.0902  $\text{H}_2\text{O}$ .  $\text{C} = 64.9$ ;  $\text{H} = 8.7$ .

$\text{C}_{10}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 65.2$ ;  $\text{H} = 8.7$  per cent.

This substance is undoubtedly identical with the *ketolactone*,  $\text{C}_{10}\text{H}_{16}\text{O}_3$  (m. p.  $62$ — $63^{\circ}$ ), which was isolated as a product of the oxidation of terpineol by chromic acid by Wallach, and has been further studied by him, as also by Tiemann and others (*Annalen*, 1893, 275, 153; 277, 118; *Ber.*, 1895, 28, 1773, 1781).

The sodium carbonate solution from which the ethereal solution of the above ketolactone had been separated was acidified with hydrochloric acid, and shaken out several times with ether. The

etheral solution was washed once with water, dried with calcium chloride, and the ether removed by distillation. The residue was a light yellow syrup, which, on standing, deposited a crystalline acid. The syrup was consequently diluted with ether, in which the crystals appeared to be sparingly soluble, and from which they were easily separated by filtration. After washing with dry ether, the substance was finally recrystallised from boiling ether. It melted at 173—174° and dissolved with effervescence in a cold solution of sodium carbonate.

0.1168 gave 0.2266  $\text{CO}_2$  and 0.0695  $\text{H}_2\text{O}$ .  $\text{C} = 52.9$ ;  $\text{H} = 6.6$ .

$\text{C}_7\text{H}_{10}\text{O}_4$  requires  $\text{C} = 53.2$ ;  $\text{H} = 6.3$  per cent.

This acid is evidently identical with *terebic acid*,  $\text{C}_7\text{H}_{10}\text{O}_4$  (m. p. 175°), which has been found as a direct oxidation product of terpineol, as also of the ketolactone,  $\text{C}_{10}\text{H}_{16}\text{O}_3$  (Tiemann and Mahla, *Ber.*, 1896, 29, 2621). The syrup from which the terebic acid crystallised was not examined but probably contained terpenylic acid, which always accompanies terebic acid when terpineol or the ketolactone is oxidised with chromic acid mixture. It is thus shown that the fractions of the oil which served for the identification of borneol also contained a considerable amount of *terpineol*.

In the first investigation of asarum oil, a considerable fraction was collected at 222—226°, and as a portion of this was still available it was thought of interest to examine it again. It was therefore oxidised with a chromic acid mixture in the manner just described, and among the products of oxidation there were isolated and identified: camphor (m. p. 175°); the ketolactone,  $\text{C}_{10}\text{H}_{16}\text{O}_3$  (m. p. 62°); and terebic acid (m. p. 173—174°). It therefore contained borneol and terpineol, and, apparently, a small amount of geraniol, as it had the characteristic rose-like odour.

#### *Identification of Terpineol.*

*Fraction 216—222°.*—This was a small fraction. It had a camphoraceous and also a somewhat rose-like odour. It was analysed and its physical constants were determined, with the following results:

0.1647 gave 0.4682  $\text{CO}_2$  and 0.1698  $\text{H}_2\text{O}$ .  $\text{C} = 77.5$ ;  $\text{H} = 11.4$ .

0.1633 „ 0.4610  $\text{CO}_2$  „ 0.1680  $\text{H}_2\text{O}$ .  $\text{C} = 77.0$ ;  $\text{H} = 11.4$ .

$\text{C}_{10}\text{H}_{18}\text{O}$  requires  $\text{C} = 77.9$ ;  $\text{H} = 11.7$  per cent.

$d_{15.5^\circ/15^\circ} = 0.9267$ ;  $n_D = -8.26'$  in a 100 mm. tube.

The portion of this fraction which had not been used in connection with the preceding one, as described under the latter, was employed for the direct identification of terpineol. In view of the presence of small amounts of other alcohols, the following method was employed.

The liquid was shaken with a concentrated solution of hydriodic acid (sp. gr. 2.0), when a heavy, dark oil was formed. This was separated from the aqueous layer, and shaken with a dilute solution of sodium bisulphite to remove any free iodine. The oil was then washed with water and allowed to stand, when after a short time crystals began to form, and finally the whole became a crystalline paste. This was spread on a porous tile, when a small quantity of nearly white needles was obtained, which, after recrystallisation from light petroleum (b. p. 30–40°), melted at 80°. This melting point was identical with that of dipentene dihydriodide,  $C_{10}H_{18}I_2$ , which, for the purpose of comparison, we had also prepared from pure crystallised terpineol, and when the two hydriodides were intimately mixed, the melting point remained unchanged. The formation of this derivative, and of the products of oxidation described in the preceding section, proves conclusively the presence of *terpineol* in the oil. The optical rotation of the fraction from which it was obtained indicates it to be the *l*-form.

#### *Identification of Geraniol.*

*Fraction 222–235°.*—This fraction was collected within the above limits, in view of the possible presence of both citronellol and geraniol. It was relatively small in amount, and was analysed, and its physical constants were determined, with the following results:

0.1544 gave 0.4370  $CO_2$  and 0.1549  $H_2O$ . C = 77.2; H = 11.1.

0.1420 „ 0.3999  $CO_2$  „ 0.1433  $H_2O$ . C = 76.8; H = 11.2.

$C_{10}H_{18}O$  requires C = 77.9; H = 11.7 per cent.

$d_{15.5^\circ/15^\circ} = 0.9340$ ;  $n_D = -9.8'$  in a 100 mm. tube.

It possessed a camphoraceous and also a fragrant, rose-like odour. Although its high density and rotation indicated that it contained a considerable amount of terpineol, and its analysis also showed an admixture with some of the next higher fraction, the small amount of liquid precluded its further purification by simple distillation.

The odour of this fraction afforded such convincing evidence of the presence of geraniol that Erdmann's method, which depends on the formation of the crystalline geranioldiphenylurethane (m. p. 82°), was resorted to for the identification of the substance (*J. pr. Chem.*, 1897, [ii], 56, 8). The oil was treated with diphenylcarbamic chloride in presence of pyridine, as described by Erdmann; the syrupy residue left after distilling the product with steam was then purified by extraction with ether, and the ethereal solution evaporated after extraction with dilute hydrochloric acid. The residual light brown oil was mixed with a little alcohol, when it soon formed a crystalline paste, which was drained on a porous tile. The substance was finally recrystallised

from a little alcohol, from which it separated in fine, glistening needles melting sharply at 81—82°. On analysis:

0.1444 gave 0.4163  $\text{CO}_2$  and 0.1015  $\text{H}_2\text{O}$ .  $\text{C} = 78.6$ ;  $\text{H} = 7.8$ .

$\text{C}_{28}\text{H}_{27}\text{O}_2\text{N}$  requires  $\text{C} = 79.1$ ;  $\text{H} = 7.7$  per cent.

The fraction by gentle oxidation with chromic acid afforded a little citral, but although the amount of the latter was too small for conversion into the naphthacinchonic acid derivative, the evidence was already sufficiently conclusive of the presence of *geraniol* in this fraction of the oil. There was, on the other hand, no indication of the presence of citronellol.

It may be noted that in the first investigation of asarum oil by one of us, a fraction was obtained corresponding approximately in boiling point (222—226°) to that just described, and that this, on more energetic oxidation with chromic acid, afforded, besides acetic acid, a small amount of a crystallisable acid. As a specimen of the latter had been preserved, it has been re-examined and shown to be a mixture of terebic and terpenylic acids.

*Fraction 235—245°*.—This was very small in amount, and was evidently a mixture of the preceding and following fractions; a little of the crystallised geranioldiphenylurethane was obtained from it by the method previously described.

#### *Identification of Eugenol Methyl Ether.*

*Fraction 245—260°*.—This constitutes the largest fraction of the oil. On redistillation under the ordinary pressure it was easily resolved into a large fraction, which was collected between 250° and 256°, but distilled for the most part between 252° and 254°. It is a colourless, nearly odourless liquid, and was analysed, and its physical constants were determined, with the following results:

0.1648 gave 0.4522  $\text{CO}_2$  and 0.1238  $\text{H}_2\text{O}$ .  $\text{C} = 74.8$ ;  $\text{H} = 8.3$ .

$\text{C}_{11}\text{H}_{14}\text{O}_2$  requires  $\text{C} = 74.2$ ;  $\text{H} = 7.9$  per cent.

$d_{15^\circ/16^\circ} = 1.0239$ ;  $n_D = -2^\circ 44'$  in a 100 mm. tube.

It has been shown by Petersen (*Ber.*, 1888, 21, 1064) that the oil obtained from the allied European species of *Asarum* contains a substance of the same composition, boiling at about 250°, which on oxidation affords veratric acid, and was fully identified as eugenol methyl ether. In the first investigation of the oil of *Asarum canadense* by one of us, a fraction was collected at 254—257°, which on oxidation with chromic acid afforded a small amount of a crystalline acid,  $\text{C}_9\text{H}_{10}\text{O}_4$ , and this Petersen has likewise found to be identical with veratric acid. The same specimen of acid, after recrystallisation from water, we now find to soften at 172°, and to melt completely at 177—178°.

The confirmation of the identity of this fraction with eugenol methyl ether has now been effected by the preparation of the crystalline bromoeugenol methyl ether dibromide,  $C_6H_2Br(OCH_3) \cdot C_3H_5Br_2$ , which melts at  $78-79^\circ$  (Wasserman, *Compt. rend.*, 1879, 88, 1206). This was accomplished as follows: To the liquid dissolved in dry chloroform, and cooled in a mixture of ice and salt, the requisite quantity of bromine, also dissolved in chloroform, was added, drop by drop, and any slight excess of bromine removed afterwards by shaking the solution with a little sulphurous acid. The chloroform solution was separated, dried, and filtered, and the chloroform removed by rapidly drawing dry air through the solution. The residue was a thick syrup, which, when dissolved in alcohol, deposited a quantity of glistening crystals. These, on recrystallisation from absolute alcohol, separated in glistening, felt-like needles, which melted at  $78-79^\circ$ .

The optical activity of the fraction is due to admixture with a small amount of a higher fraction, which it is difficult to separate completely by fractional distillation.

*Search for isoEugenol Methyl Ether.*—As it has been assumed by Mittmann (*Arch. Pharm.*, 1889, 227, 543) that the substance contained in asarum oil is not eugenol methyl ether but the isomeride, we have thought it desirable to ascertain the correctness of this opinion. For this purpose, a portion of the original oil which had been deprived of terpene was fractionated under diminished pressure before being subjected to hydrolysis. As eugenol methyl ether boils at  $128-130^\circ$  (10 mm.) and isoeugenol methyl ether at  $142^\circ$  (10 mm.), fractions were first collected at  $130-140^\circ$  and at  $140-155^\circ$  under a pressure of about 10 mm. Further fractionation was conducted under 60 mm. pressure, at which eugenol methyl ether was found to boil at  $166^\circ$ , and isoeugenol methyl ether at  $179^\circ$ . A large fraction was thus collected at  $163-167^\circ$  (60 mm.), and also a fraction at  $175-185^\circ$  (60 mm.). For the differentiation of these two substances recourse was had to bromination, as eugenol methyl ether in the cold yields the bromo bromide, whereas isoeugenol methyl ether under the same conditions yields only a dibromide melting at  $99-101^\circ$  (*Ber.*, 1890, 23, 1167). On applying this test to the two fractions, only the crystalline derivative melting at  $78-79^\circ$  was obtained, which proves that the original oil does not contain isoeugenol methyl ether.

#### *Fraction boiling above $260^\circ$ .*

This fraction was distilled under reduced pressure, and after a large number of distillations under 60 mm. pressure the following fractions were obtained: Below  $175^\circ$ ,  $175-195^\circ$ ,  $195-210^\circ$ ,  $210-220^\circ$ , and  $220-230^\circ$ .

The characters of these fractions are shown in the following table :

Boiling point (60 mm.).	Analysis.	Rotation in 100 mm. tube.	Solubility in 70 per cent. alcohol.	Colour.
Below 175°	—	—	Very freely soluble	Slight
175—195	C=76.0 ; H= 9.3	$\alpha_D = -10^{\circ}12'$	Very freely soluble	Light yellow
195—210	C=78.4 ; H=10.3	$\alpha_D = -41.40$	Very freely soluble	Bluish
210—220	C=81.1 ; H=10.5	$\alpha_D = -100$	Less freely soluble	Bluish
220—230	—	—	Turbid	Greenish

The fraction collected below 175° consisted chiefly of eugenol methyl ether. The three subsequent fractions had an odour resembling that of cedar wood, and when a few drops were dissolved in glacial acetic acid and a drop of concentrated hydrochloric or sulphuric acid added, an intense reddish-violet colour was produced. The fraction 220—230° was very small in amount. The analysis of the principal fractions, and particularly their ready solubility in dilute alcohol, proved that they consisted of oxygenated compounds, and did not contain a sesquiterpene.\* As the fraction 210—220° was the largest, this was again carefully distilled, and the following fairly constant fraction obtained, which was more fully examined.

*Fraction 212—217° (60 mm.).*—This is a thick, viscid liquid, having a fine blue colour and an odour recalling that of cedar wood. It does not solidify when exposed for some time to a temperature of  $-18^{\circ}$ . It is very freely soluble in 70 per cent. alcohol and affords the same colour reaction as the fraction from which it was obtained. It was analysed, and its physical constants were determined, with the following results :

0.1069 gave 0.3133  $\text{CO}_2$  and 0.1009  $\text{H}_2\text{O}$ . C=79.9 ; H=10.5.  
 $d_{15^{\circ}/16^{\circ}} = 1.0063$  ;  $\alpha_D = -3^{\circ}$  ;  $l = 100$  mm ;  $c = 3.678$  ;  $[\alpha]_D = -81.5^{\circ}$ .

A molecular weight determination gave the following result : 0.4184 gram depressed the freezing point of 30.17 grams of phenol by  $0.48^{\circ}$ , whence mol. wt. = 214.

This result would agree very well with a sesquiterpene alcohol of the formula  $\text{C}_{15}\text{H}_{26}\text{O}$  (mol. wt. = 222), but the analytical figures do not accord with those required for this substance (C=81.1 ; H=11.7 per cent.). It is probable, therefore, that the fraction analysed still consisted of more than one substance.

\* The statement in "The Volatile Oils," by Gildemeister and Hoffmann (p. 123) that "Semmler, in 1889, obtained from asarum oil a hydrocarbon,  $\text{C}_{15}\text{H}_{24}$ , boiling at about  $255^{\circ}$ " is an error of translation. It properly refers to the oil of *Carlina acaulis* or Carline thistle (German, *Eberwurz*), which is described on p. 690 of the same work.



*Treatment with Phosphoric Oxide.*—In order to obtain further evidence respecting the character of these bluish fractions, an attempt was made to dehydrate them. The remainder of the fractions 195—210° and 210—220° (60 mm.), about 5 grams of each, was separately dissolved in dry benzene, phosphoric oxide added, and the liquids boiled for about an hour, when they acquired a deep purple-red colour. After distilling off the benzene, the residues were distilled under diminished pressure.

*Fraction 195—210° (60 mm.)* afforded a liquid which distilled between 175° and 210° under 60 mm. pressure. It had a bright green colour, a cedar-like odour, and was insoluble in 70 per cent. alcohol.

0.1068 gave 0.3198  $\text{CO}_2$  and 0.1000  $\text{H}_2\text{O}$ .  $\text{C} = 81.7$ ;  $\text{H} = 10.4$  per cent.  
 $d_{15^\circ/15^\circ} = 0.975$ ;  $[\alpha]_D = -37^\circ$ .

*Fraction 210—220° (60 mm.)* afforded a liquid which distilled chiefly between 200° and 220° under 60 mm. pressure. It had an olive-green colour, a cedar-like odour, and was insoluble in 70 per cent. alcohol.

0.1073 gave 0.3300  $\text{CO}_2$  and 0.1006  $\text{H}_2\text{O}$ .  $\text{C} = 83.9$ ;  $\text{H} = 10.4$  per cent.  
 $d_{15^\circ/15^\circ} = 0.985$ ;  $[\alpha]_D = -35.5^\circ$ .

Both these liquids, when dissolved in glacial acetic acid and treated with a drop of hydrochloric acid, afforded a purplish or red colour. Although the insolubility of these products in alcohol and the increase in the percentage of carbon by the above treatment was evidence of the formation of a hydrocarbon, the substances themselves were not sufficiently pure to admit of further identification. They were finally dissolved in dry ether, the solutions saturated with dry hydrogen chloride, and allowed to stand for several days, but from the very dark, oily residues no crystallisable hydrochloride could be obtained.

Although several essential oils are known to afford high boiling fractions of a deep blue colour, which have been designated as *cærulein* by Gladstone, and as *azulene* by Piesse, no properly characterised compound has as yet been isolated from any one of them.

#### *Acids obtained by the Hydrolysis of the Oil.*

The strongly alkaline, aqueous liquid, separated from the hydrolysed oil and completely extracted with ether, as previously described, was evaporated to a small bulk, then acidified with sulphuric acid and distilled with steam. The first portion of the distillate was slightly turbid, but it soon became clear. The entire acid liquid was then made alkaline with sodium carbonate, and extracted several times with ether. After distilling off the ether there remained a small amount of a dark coloured, highly aromatic oil. This was insoluble

in a cold solution of sodium hydroxide, but dissolved readily on warming. The alkaline solution of the substance was shaken with ether to remove any impurity, and then acidified with sulphuric acid, which liberated the original oil. This was again taken up with ether, the ethereal solution washed with a little water, dried, evaporated, and the slightly coloured, oily residue finally placed in a vacuum desiccator over paraffin to remove the last traces of ether, and then analysed.

0.0463 gave 0.1292  $\text{CO}_2$  and 0.0403  $\text{H}_2\text{O}$ .  $\text{C} = 76.1$ ;  $\text{H} = 9.7$ .

$\text{C}_{14}\text{H}_{20}\text{O}_2$  requires  $\text{C} = 76.4$ ;  $\text{H} = 9.1$  per cent.

This substance, to which we assign the provisional formula  $\text{C}_{14}\text{H}_{20}\text{O}_2$ , is evidently a *lactone*. Although existing in extremely small amount, so that we have not been able to examine it further, its powerful odour indicates that it must have considerable influence on the odour of the original oil. To it is also possibly due the somewhat clove-like odour which was observed in the isolation of the phenol (p. 60).

After the lactone had been separated from the liquid which had been made alkaline with sodium carbonate, this liquid was concentrated, strongly acidified with sulphuric acid, and shaken four times successively with ether. The ethereal solution was washed twice with water, dried, and distilled. On fractionating the residue, nearly all distilled between  $110^\circ$  and  $120^\circ$ . A portion of this was converted into the barium salt, and from the latter the silver salt was prepared which gave the following figures on analysis:

0.085 gave on ignition 0.0550 Ag.  $\text{Ag} = 64.7$ .

$\text{C}_2\text{H}_3\text{O}_2\text{Ag}$  requires  $\text{Ag} = 64.7$  per cent.

This served to confirm the presence of *acetic acid*, the previous investigation having shown that esters of this acid were present in considerable amount in the oil.

*Acids of Higher Boiling Point.*—The residue from the distillation of the acetic acid was very small in amount, and was therefore mixed with a larger portion of acids obtained by shaking the original oil with a solution of sodium carbonate. The whole of the acids of higher boiling point, after standing over potash in a vacuum desiccator, was first fractionated under 10 mm., and then under the ordinary pressure, when the following three fractions were obtained.

(1) Below  $240^\circ$ ; (2)  $240-280^\circ$ ; (3)  $280-300^\circ$ .

The last fraction became solid on standing, and from the residue in the flask crystals were separated which, after recrystallisation from hot light petroleum, melted at  $57-58^\circ$ ; these consisted apparently of palmitic acid, which had been extracted by means of caustic alkali from the original oil. The first two fractions were redistilled and the follow-

ing fractions collected : A, 140—200 ; B, 200—230° ; C, 230—270°.  
D was fraction (3) from the first distillation (b. p. 280—300°).

They were yellowish, oily liquids, nearly equal in amount, and were present altogether to the extent of about 2 grams in a kilo. of the original oil. They were first converted into ammonium salts, and then fractionally precipitated by silver nitrate. The various silver salts were spread on porous plates, and then dried at 80° for half-an-hour. On analysis, they gave the following results :

A<sub>1</sub>. Ag = 46.1 per cent. ; A<sub>2</sub>. Ag = 48.4 per cent.

B<sub>1</sub>. Ag = 45.1       ,,       B<sub>2</sub>. Ag = 47.1       ,,

C<sub>1</sub>. Ag = 36.7       ,       C<sub>2</sub>. Ag = 39.5       ,,

D<sub>1</sub>. Ag = 34.5       ,,       D<sub>2</sub>. Ag = 39.2       ,,

C<sub>6</sub>H<sub>11</sub>O<sub>2</sub> Ag requires Ag = 48.4. C<sub>12</sub>H<sub>23</sub>O<sub>2</sub> Ag requires Ag = 35.1 percent.

It is thus seen that these acids of high boiling point constitute an exceedingly complicated mixture, the amounts of silver found corresponding to those required for salts of acids ranging from C<sub>6</sub>H<sub>11</sub>O<sub>2</sub> to C<sub>12</sub>H<sub>23</sub>O<sub>2</sub>. A further separation and identification of them would require a very much larger quantity of material than was available for the purpose. It may also be noted that from the method by which the chief portion of these acids was obtained, it is evident that they exist in the oil in a free state, and not in the form of esters.

### Summary.

From the results of this investigation, the oil of *Asarum canadense* is seen to contain the following substances :

1. A phenol, C<sub>6</sub>H<sub>11</sub>O<sub>2</sub>,
2. Pinene, apparently a mixture of the *d*- and *l*-forms,
3. *d*-Linalool,
4. *l*-Borneol,
5. *l*-Terpineol,
6. Geraniol,
7. Eugenol methyl ether,
8. A blue oil, of undetermined composition, consisting of oxygenated substances of alcoholic nature,
9. A lactone, C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>,
10. Palmitic acid,
11. Acetic acid, and
12. A mixture of fatty acids intermediate between acetic and palmitic acids.

In order to ascertain approximately the amounts of the principal constituents, the following determinations were made with the original oil :

1. The eugenol methyl ether was determined by Zeisel's method. 0.1898 gram of oil gave 0.1846 gram AgI, whence eugenol methyl ether = 36.9 per cent.
2. The amount of esters, calculated as  $C_{10}H_{17} \cdot C_2H_3O_2$ , is 27.5 per cent.
3. The total amount of alcohols,  $C_{10}H_{18}O$ , free and as esters, after acetylating the hydrolysed oil, was found to be 34.9 per cent., hence the amount of free alcohols is 13.3 per cent. In reality, the amount of free alcohols is somewhat larger than this, as it is known that linalool and terpineol cannot be quantitatively acetylated.
4. As about 2 per cent. of pinene was found in the oil, the constituents of high boiling point, blue oil, &c., would amount to somewhat less than 20 per cent.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES.

### VIII.—*Derivatives of Gallic Acid.*

By FREDERICK B. POWER and FRANK SHEDDEN.

IN a paper entitled: "The Chemical Character of so-called Iodotannin Compounds" (*Pharm. Journ.*, 1901, [iv], 13, 147), the authors have recorded the results of an investigation which was undertaken for the purpose of ascertaining the character of the compounds prepared by the direct action of iodine on tannic acid in the presence of water. It was shown that under these conditions no definite compound of either tannic or gallic acid with iodine could be formed, and it therefore seemed of interest to ascertain whether iodine could be introduced into the gallic acid molecule by indirect methods. With this object in view, the following method of procedure was adopted. The well-crystallised ethyl gallate was converted into its triacetyl derivative, which, on nitration, yielded *ethyl dinitrodiacetyl gallate*. This substance, on hydrolysis with sulphuric acid, was converted into *ethyl dinitrogallate*, and from the latter, on reduction, *ethyl monoaminogallate* and *ethyl diaminogallate* were obtained in the form of hydrochlorides. These hydrochlorides were then separately diazotised, and the resulting solutions boiled with potassium iodide in accordance with the well-known reaction. Although many experiments were made, it was not possible to isolate any product containing iodine.

As most of the substances required for the original purpose of this investigation represent new derivatives of gallic acid, the method of preparation and their characters are here described.

*Ethyl Dinitrodiacetylgallate*,  $C_6(NO_2)_2(C_2H_3O_2)_2(OH) \cdot CO_2C_2H_5$ .

By the direct acetylation of ethyl gallate, the ethyl triacetylgallate was first prepared, which has been described by Schiff (Beilstein's *Handbuch*, 2, 1922) as a thick yellow oil, which very slowly deposits crystals. No difficulty was experienced, however, in obtaining it in colourless crystals from either acetic acid or alcohol. It melts at  $133^\circ$ . The triacetyl ester was nitrated in the following manner. One hundred grams of the triacetyl ester were added to a cold mixture of 50 c.c. each of nitric acid (sp. gr. 1.42) and sulphuric acid, and 150 c.c. of glacial acetic acid. The mixture, while being kept cool, was allowed to stand for five hours. The product was poured into a litre of water, the yellow, crystalline precipitate filtered off, and the nitro-compound separated from some unchanged ethyl triacetylgallate by treatment with sodium carbonate, in which it readily dissolved. The acid filtrate from the above-mentioned yellow precipitate was extracted several times with ether and the ethereal liquid shaken out with carbonate solution. This was mixed with the main sodium carbonate solution obtained as above and the whole acidified with hydrochloric acid. The separated yellow oil soon formed a crystalline cake, which was collected and recrystallised from chloroform. It formed lemon-yellow needles which melted at  $165^\circ$ .

0.1466 gave 0.2260  $CO_2$  and 0.0486  $H_2O$ .  $C = 42.0$ ;  $H = 3.7$ .

0.1974 „ 13.3 c.c. moist nitrogen at  $11^\circ$  and 744 mm.  $N = 7.9$ .

$C_{18}H_{12}O_{11}N_2$  requires  $C = 41.9$ ;  $H = 3.2$ ;  $N = 7.5$  per cent.

The substance is strongly acid, dissolving in sodium carbonate with effervescence and forming an orange-red solution. It only dissolves slowly in absolute alcohol, and the solution gives a bluish-green coloration with ferric chloride.

The ethyl triacetylgallate was nitrated in another manner with somewhat different results. One hundred grams of the substance were mixed in a flask with 100 c.c. of nitric acid (sp. gr. 1.42), and, after being kept cool for five hours, the mixture was worked up in the manner already described. By this method, the product consisted of a mixture of the dinitro-ester and the dinitrodiacetyl ester.

An attempt was made to form the sodium salt of ethyl dinitrodiacetylgallate by dissolving it in alcohol and adding one atomic proportion of sodium dissolved in a little alcohol. No precipitate was produced, even after a portion of the alcohol had been evaporated off in a vacuum. On standing for several days, an odour of ethyl acetate was developed, and small, bright red crystals were deposited, which consisted of the sodium salt of *ethyl dinitrogallate*.

*Ethyl Dinitrotriacylgallate*,  $C_6(NO_2)_2(C_2H_5O_2)_3 \cdot CO_2C_2H_5$ .

This was prepared by the acetylation of the dinitrodiacetyl compound, in the formation of which one acetyl group had become eliminated during the process of nitration. It was obtained in colourless needles, which gradually become yellow, and melt at 145—146°.

0.1716 gave 0.2704  $CO_2$  and 0.0504  $H_2O$ . C = 43.0; H = 3.3.

0.2086 „ 12.4 c.c. moist nitrogen at 16° and 768 mm. N = 7.0.

$C_{15}H_{14}O_{12}N_2$  requires C = 43.5; H = 3.4; N = 6.8 per cent.

The substance was insoluble in sodium carbonate. Its cold alcoholic solution gave no reaction with ferric chloride, but on boiling, a bluish-green colour was produced.

*Ethyl Dinitrogallate*,  $C_6(NO_2)_2(OH)_3 \cdot CO_2C_2H_5$ .

This was prepared by boiling the dinitrodiacetyl compound with 50 per cent. sulphuric acid, when it crystallised out on cooling. The ethyl radicle was not eliminated by this procedure.

It was obtained in the form of small, yellow scales, of a somewhat deeper colour than the dinitrodiacetyl compound. When placed in the melting point apparatus at 80—85° it melted, but after drying at a gentle heat it fused at 153°.

0.8040 air-dried substance lost 0.0486  $H_2O$  at 100°.  $H_2O$  = 6.0.

$C_6(NO_2)_2(OH)_3 \cdot CO_2C_2H_5 \cdot H_2O$  requires  $H_2O$  = 5.9 per cent.

It was recrystallised by dissolving the dried substance in absolute ether and adding an equal volume of light petroleum. The crystals, after drying for a few minutes in a water-oven, softened at 151° and melted to a clear liquid at 153—154°.

0.1432 gave 0.1990  $CO_2$  and 0.0382  $H_2O$ . C = 37.9; H = 3.0.

0.1662 „ 14.4 c.c. moist nitrogen at 20° and 759 mm. N = 9.9.

$C_9H_8O_9N_2$  requires C = 37.5; H = 2.7; N = 9.7 per cent.

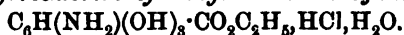
The substance dissolves readily in absolute alcohol, and the solution gives an olive-green colour with ferric chloride. It could not be hydrolysed by heating in a sealed tube with hydrochloric acid at 125° for six hours. It was also heated in a sealed tube with 50 per cent. sulphuric acid at 155° for five hours without altering the melting point or other properties. Ethyl gallate, on the other hand, when heated in a sealed tube with 30 per cent. sulphuric acid at 150°, is completely hydrolysed. On boiling with an excess of alcoholic sodium hydroxide, the substance was destroyed. It was treated with strong ammonia in the hope of forming the amide, but only tarry products were obtained.

*Reduction of Ethyl Dinitrogallate.*—The crude nitro-compound was reduced by warming with tin and hydrochloric acid. After the reaction was over, the liquid was diluted with water and the tin completely removed by hydrogen sulphide. The clear liquid was distilled in a vacuum, and, when it had become concentrated to a small bulk, white, needle-shaped crystals began to separate out. The distillation was then stopped and the crystalline precipitate filtered off and washed with dilute hydrochloric acid. This substance proved to be the *hydrochloride of ethyl monoaminogallate*. The yield was about 12 per cent. of the original substance.

The filtrate and washings were evaporated to complete dryness in a vacuum. The residue was a crystalline mass, which was purified by dissolving it in hot methyl alcohol and diluting the solution with hot chloroform. A light brown or nearly white, crystalline powder was thus obtained, which consisted of the *hydrochloride of ethyl diamino-gallate*. The yield of the latter was very variable, ranging from about 10 to 25 per cent. of the original substance.

The formation of the above monoamino-derivative by reduction was at first thought to be due to the presence of a mononitro-ester in the material used. This, however, was not the case, inasmuch as a pure ethyl dinitrodiacetyl-gallate afforded the same yield of the monoamino-hydrochloride. The conclusion may thus be drawn that the formation of the monoamino-derivative is due to some change in the process of reduction.

*Hydrochloride of Ethyl Monoaminogallate,*



This substance has the following characters. It is readily soluble in water and the solution remains colourless. Its alcoholic solution gives a dark green colour with ferric chloride. It melts at  $210^\circ$  with blackening and frothing. When recrystallised by dissolving it in hot absolute alcohol and adding chloroform to the solution, it still melted at  $210^\circ$ , and was quite white, showing no tendency to change on keeping. When dissolved in a little water, it could be precipitated by the addition of strong hydrochloric acid, and this reaction, besides the other characters of the substance, distinguishes it from the diamino-gallate. It may be heated in a water-oven without any change in weight.

0.1186 gave 0.1760  $\text{CO}_2$  and 0.0540  $\text{H}_2\text{O}$ .  $\text{C} = 40.5$ ;  $\text{H} = 5.05$ .

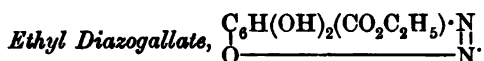
0.1290 „ 0.1908  $\text{CO}_2$  „ 0.0586  $\text{H}_2\text{O}$ .  $\text{C} = 40.3$ ;  $\text{H} = 5.05$ .

0.1724 „ 8.8 c.c. moist nitrogen at  $24^\circ$  and 753 mm.  $\text{N} = 5.65$ .

0.1950 „ 0.1058 gram  $\text{AgCl}$ .  $\text{Cl} = 13.4$ .

0.5504 at  $105^\circ$  lost 0.0392  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 7.1$ .

$\text{C}_6\text{H}_{11}\text{O}_5\text{N}, \text{HCl}, \text{H}_2\text{O}$  requires  $\text{C} = 40.4$ ;  $\text{H} = 5.2$ ;  $\text{N} = 5.2$ ;  $\text{Cl} = 13.3$ ;  
 $\text{H}_2\text{O} = 6.7$  per cent.



The ethyl monoaminogallate was dissolved in an excess of dilute hydrochloric acid, and to the ice-cold solution a dilute solution of sodium nitrite was slowly added until there was a permanent excess. The liquid was heated on a water-bath for 20 minutes, and, after cooling, the brown crystals were filtered off.

The product was almost insoluble in cold water, but dissolved in boiling water, and on cooling the solution long, orange-yellow needles were deposited. The solution was yellow, and gave a deep purplish-brown colour with ferric chloride. The substance melted with sudden decomposition at  $182^\circ$ . When recrystallised from dilute acetic acid, it formed fine, reddish-brown needles melting as before at  $182^\circ$ .

0.2350 at  $100^\circ$  lost 0.0178  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 7.6$ .

$\text{C}_9\text{H}_8\text{O}_5\text{N}_2 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 7.4$  per cent.

The dried substance was analysed with the following result :

0.1108 gave 0.1938  $\text{CO}_2$  and 0.0432  $\text{H}_2\text{O}$ .  $\text{C} = 47.7$  ;  $\text{H} = 4.3$ .

0.0924 „ 10 c.c. moist nitrogen at  $24^\circ$  and 769 mm.  $\text{N} = 12.3$ .

$\text{C}_9\text{H}_8\text{O}_5\text{N}_2$  requires  $\text{C} = 48.2$  ;  $\text{H} = 3.5$  ;  $\text{N} = 12.5$  per cent.

0.1114 gram dissolved in 15.59 grams of pure phenol depressed the freezing point by  $0.263^\circ$ . This corresponds to a molecular weight of 201. Mol. wt. of  $\text{C}_9\text{H}_8\text{O}_5\text{N}_2 = 224$ .

One gram of the substance was heated with three times its weight of water in a sealed tube at  $220^\circ$  for four hours, when complete solution was effected. The dark brown liquid was filtered from a small amount of a black residue, saturated with ammonium sulphate, and extracted with ether. The ethereal solution, when washed with water, dried with sodium acetate, and evaporated, left a yellowish, oily liquid which became crystalline. The crystals, after washing with a little light petroleum, melted at  $139^\circ$ , and were free from nitrogen. Their aqueous solution gave a brown colour with alkalis and a bluish-black one with ferric chloride. After recrystallising this from toluene, about 0.2 gram of the substance was obtained, and it then melted at  $140^\circ$  without decomposition. It was dried in a water-oven and then analysed :

0.1084 gave 0.2174  $\text{CO}_2$  and 0.0504  $\text{H}_2\text{O}$ .  $\text{C} = 54.7$  ;  $\text{H} = 5.2$ .

$\text{C}_9\text{H}_{10}\text{O}_5$  requires  $\text{C} = 54.5$  ;  $\text{H} = 5.1$  per cent.

The substance thus produced was therefore undoubtedly ethyl gallate, the nitrogen having been completely eliminated by heating the diazogallate with water.



On treating the diazo-compound with stannous chloride in cold hydrochloric acid, considerable effervescence was produced and it became completely dissolved. After removing the tin by hydrogen sulphide, the products of the reaction were found to be ammonium chloride and ethyl gallate. The production of ethyl gallate from this diazo-compound will serve to explain the formation of the monoamino-ester by the reduction of ethyl dinitrogallate (p. 76).

*Hydrochloride of Ethyl Diaminogallate,*  
 $C_6(NH_2)_2(OH)_3 \cdot CO_2C_2H_5, 2HCl.$

This substance, as obtained in the manner already described, forms a fine, crystalline powder of a light brown colour. By redissolving it in hot absolute alcohol (in which it is somewhat sparingly soluble) and adding ethyl acetate it becomes much lighter in colour, but when kept shows a tendency to darken. The alcoholic solution rapidly assumes a pink hue. It is very easily oxidised. It dissolves readily in water, but the solution almost immediately becomes blue, and, on standing, blue flakes are deposited. The blue colour is intensified by the cautious addition of ferric chloride, but is destroyed by adding an excess. If the solution in water be acidified with hydrochloric acid, the blue colour changes to pink (compare *Ber.*, 1887, 20, 335; 1893, 26, 2184). Unlike ethyl monoaminogallate, it cannot be precipitated from its aqueous solution by hydrochloric acid. It melts with decomposition at 197°. After drying in a vacuum, it was analysed.

0.1318 gave 0.1738  $CO_2$  and 0.0570  $H_2O$ . C = 35.9; H = 4.8.

0.1330 „ 0.1746  $CO_2$  „ 0.0538  $H_2O$ . C = 35.7; H = 4.5.

0.2129 „ 19.6 c.c. moist nitrogen at 23° and 764 mm. N = 10.4.

0.1588 „ by Carius' method, 0.1520  $AgCl$ . Cl = 23.7.

$C_9H_{12}O_5N_2, 2HCl$  requires C = 35.9; H = 4.6; N = 9.3; Cl = 23.6 per cent.

In order to ascertain the action of nitrous acid on this diamino-ester, 6.6 grams of the substance were mixed with an excess of dilute hydrochloric acid. The resulting dark coloured solution was cooled with water and a dilute solution of sodium nitrite gradually added, which caused considerable effervescence and the evolution of some nitrous fumes. This liquid was extracted with ether, but on distillation the latter left only a very slight residue. The remaining liquid was heated on a water-bath, when there was considerable effervescence, and, after this had ceased, a small portion of the liquid, when boiled with potassium hydroxide, evolved ammonia. The remainder was extracted with chloroform, then made alkaline with sodium carbonate and again extracted with chloroform, but in neither case was any definite product obtained.

IX.—*Thiocarbamide Hydrochloride.*

By HENRY P. STEVENS, M.A., Ph.D.

THIOCARBAMIDE hydrochloride is stated by Glutz (*Annalen*, 1870, 154, 40) to be obtained from thiocarbamide stannochloride by removal of the tin and concentration of the resulting aqueous solution, as a crystalline substance which could be purified by recrystallisation from alcohol. It was not analysed, nor was its melting point given, and the only evidence brought forward by Glutz to show that it was thiocarbamide hydrochloride is the fact that with platinic chloride it gave a double salt, and with silver nitrate a mixed precipitate of silver chloride and the silver compound of thiocarbamide.

Reynolds (*Annalen*, 1869, 150, 232) was unable to prepare the hydrochloride, whilst Claus (*Annalen*, 1875, 179, 131) states that, like Reynolds, he had been unable to prepare the hydrochloride *directly*, but had often obtained the pure salt by Glutz's method, in spite of which assertion, however, no analysis is given nor is the salt in any way further characterised. It is therefore a matter of doubt whether thiocarbamide hydrochloride has hitherto been isolated in a pure state.

On investigating the question, it was found that identical products were obtained by Glutz's method and by bringing together aqueous solutions of thiocarbamide and hydrochloric acid in the calculated proportion.

The white, crystalline substance produced on evaporation of the solutions on the water-bath is very soluble in alcohol, and when fractionally recrystallised from this solvent, it yields, in addition to some unchanged thiocarbamide, well-formed, prismatic crystals having an ill-defined melting point and containing an amount of chlorine too small for such a compound as  $\text{CS}(\text{NH}_2)_2 \cdot \text{HCl}$ . Repeated crystallisation from alcohol, instead of purifying the compound, lowered the percentage of chlorine without, at the same time, yielding any free thiocarbamide.

Eventually the hydrochloride was obtained pure by the following method. Thiocarbamide was dissolved in more than sufficient of the most concentrated, warm, aqueous hydrochloric acid to convert the whole into hydrochloride. On allowing the solution to stand, the hydrochloride separated out in thick, massive crystals. The mother liquor was poured off from the crystals, which were then redissolved by gently warming in the smallest possible quantity of hydrochloric acid, from which, on standing, the greater part again separated. It is difficult to dry the crystals without slight loss of hydrogen chloride; they may, however, be obtained in a pure state by pouring off the mother liquor, washing them rapidly with cold alcohol on the filter pump, and drying them over calcium chloride. On analysis:

I. 0.1212 gave 0.1546 AgCl. Cl = 31.54.

II. 0.2374 „ 0.3017 AgCl. Cl = 31.42.

$\text{CH}_5\text{N}_2\text{ClS}$  requires Cl = 31.38 per cent.

As thiocarbamide in aqueous solution has a neutral reaction with respect to litmus, the whole of the chlorine can be accounted for as hydrochloric acid by titration with decinormal ammonium hydroxide solution. Thus, in analysis II, the substance was titrated, before precipitation, with silver nitrate and gave Cl = 31.46 per cent.

The salt, when exposed to air, rapidly effloresces with the loss of some hydrogen chloride, of which about one-half can be removed by prolonged exposure in a vacuum over strong sulphuric acid and potassium hydroxide. When heated, it softens gradually and melts below  $100^\circ$ . It is extremely soluble in water or alcohol. If silver nitrate be gradually added to a solution of the hydrochloride, the precipitate first formed redissolves immediately in the excess of the hydrochloride solution, and on allowing the clear liquid to stand, fine, needle-shaped crystals separate out which melt at  $172^\circ$  and on oxidation with nitric acid yield silver chloride. They appear to be identical with the compound  $2\text{OS}(\text{NH}_2)_2, \text{AgCl}$  (m. p.  $170-171^\circ$ ) obtained by Reynolds (Trans., 1892, 61, 252) by dissolving silver chloride in a hot alcoholic solution of thiocarbamide.

Thiocarbamide forms additive compounds with alkyl iodides and bromides on standing in the cold or heating in sealed tubes (Claus, *Annalen*, 1875, 179, 145; Bernthsen and Klinger, *Ber.*, 1878, 11, 492, &c.); but no statement, however, is to be found with regard to its behaviour with the alkyl chlorides. On treating a solution of thiocarbamide in alcohol with ethyl chloride, freed from hydrochloric acid by bubbling through water with calcium carbonate in suspension, no appreciable action took place even on warming the solution. Nevertheless, it was possible that ethyl chloride, formed in the solution itself by the action of hydrochloric acid on the alcohol, might prove more reactive, and this was eventually found to be the case.

An alcoholic solution of thiocarbamide hydrochloride, prepared by dissolving thiocarbamide in about ten times its weight of alcohol in which the necessary amount of hydrogen chloride had been dissolved, was boiled for several days in a reflux apparatus on a water-bath. The solution was evaporated down twice with fresh quantities of alcohol to remove any slight excess of hydrochloric acid. The product, a thick, unpleasant smelling oil, solidified completely on standing and stirring with a glass rod. Like thiocarbamide hydrochloride, it was extremely soluble in water or alcohol, but insoluble in other solvents provided they were dry, and on this account much difficulty was experienced in finding a suitable solvent for its recrystallisation. Eventually the product was dissolved by gently warming and shaking in glacial acetic

acid, a few drops of water or alcohol being added to promote solution. Dry ether, insufficient in amount to cause any permanent precipitation, was then added in small quantities at a time to the cold solution, and the whole set aside to stand; a crop of crystals formed which was filtered off, and the mother liquor treated with more ether. In this manner, by a process of fractional crystallisation, the new substance was obtained in a state of purity. It is more soluble than thiocarbamide hydrochloride in the mixture of glacial acetic acid and ether, and separates when pure from the same solvent in long, slender prisms. It melts gradually just below  $100^{\circ}$ . The aqueous solution of the salt is neutral to litmus, but the whole of the chlorine is precipitated as silver chloride by silver nitrate in dilute nitric acid solution. Chlorine estimations showed that it is an additive product of thiocarbamide and ethyl chloride, or, from another point of view, that it is ethyl- $\psi$ -thiocarbamide hydrochloride.

0.2097 gave 0.2122 AgCl. Cl = 25.02.

0.2183 „ 0.2227 AgCl. Cl = 25.22.

$C_2H_5N_2ClS$  requires Cl = 25.20 per cent.

This hydrochloride behaves similarly to the hydriodide obtained by direct combination of thiocarbamide and ethyl iodide.

It follows, therefore, that thiocarbamide hydrochloride cannot be recrystallised from alcohol, as it reacts with it to give ethyl- $\psi$ -thiocarbamide hydrochloride.

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## X.—A Method for Determining Small Quantities of Carbonates.

By ALFRED DANIEL HALL and EDWARD JOHN RUSSELL.

THE determination of small quantities of carbonates in material like soil is attended with many difficulties, owing to the solubility of the carbon dioxide in the acid used for decomposing the carbonate. When the soil contains 2 per cent. or more of carbonates, calculated as calcium carbonate, Scheibler's apparatus may be used, and the empirical correction for solution of the carbon dioxide (Warrington, *Chem. News*, 1875, 31, 253) will not introduce a greater experimental error than attaches to the natural variation of the sample for analysis. But with small proportions of calcium carbonate, 0.5 per cent. and

below, Scheibler's apparatus becomes unworkable, for all the gas produced remains in the reacting acid. Gravimetric methods, where the carbon dioxide is either weighed directly or by difference, require very refined manipulation when 100 grams of soil have to be attacked by acid and the mixture boiled, &c., to obtain quantities like 0.1 gram of carbon dioxide. Working in a vacuum by ordinary gas analysis methods, the carbon dioxide can be collected and measured, but there are, again, difficulties due to solution which render the process tedious and susceptible of error.

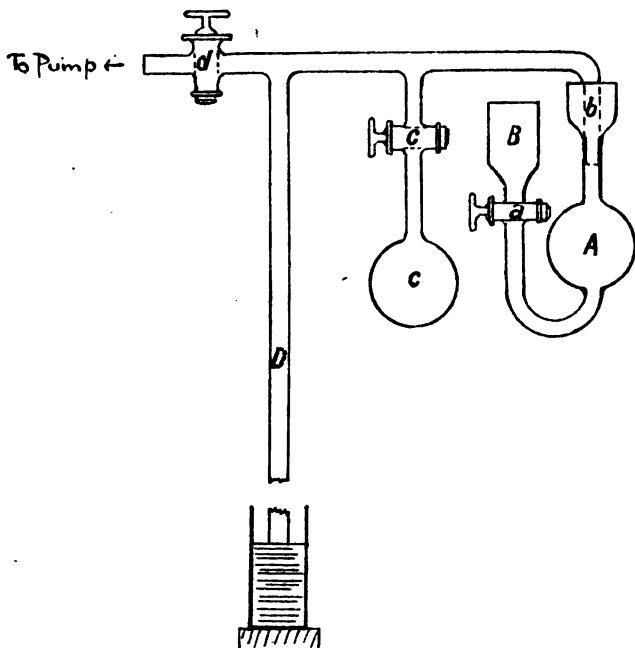
The suggestion has often been made that the soil should be treated with a known volume of standard acid, and the amount of calcium carbonate present calculated from the acid neutralised. This process, however, always gives results which are too high, owing to the fact that various humates, silicates, and in some cases ferric oxide, are also attacked by the acid without liberating any acid which affects the indicator.

Stutzer and Hartleb (*Zeit. angew. Chem.*, 1899, 12, 448) have proposed to distil the soil with a solution of ammonium chloride; the calcium carbonate present forms ammonium carbonate by double decomposition; this dissociates, and the ammonia is caught by standard acid and titrated. This method is open to all the sources of error indicated above (compare Schutte, *Zeit. angew. Chem.*, 1899, 14, 854; Woy, *Chem. Centr.*, 1899, ii, 847; and Immendorff, *Zeit. angew. Chem.*, 1900, 15, 1177).

In searching for a more workable process, the authors have devised the apparatus described below, by means of which the main source of error in determinations of carbon dioxide, its solubility, is eliminated. The process is also reasonably rapid and requires no special skill in manipulation.

The apparatus is figured on p. 83. (A) is the reaction bulb, about 60 c.c. in capacity. It is connected from below with the small funnel (B), carrying the stopcock (a). (A) is connected to the rest of the apparatus by a cup joint at (b). (C) is a second bulb, rather smaller than (A) (in the apparatus actually used, its capacity was 42.5 c.c.); on the tube connecting (C) to the rest of the apparatus is a stopcock (c). The stopcocks and cup joint must be well ground and lubricated so as to maintain a vacuum. (D) is a capillary tube 800 mm. long, dipping into a small reservoir of mercury and serving as a manometer; a third stopcock (d) is placed between the manometer and the pump. The bulbs (A) and (C) can be enclosed in a water-bath. Before the apparatus is fixed on the stand, the capacity of the bulb (C) must be ascertained with accuracy; this may be done by filling the bulb with mercury and then weighing the mercury when shaken out and collected.

Two to 10 grams of the substance in a finely powdered state are introduced into (*A*) and covered with water, the cup joint is wiped, well lubricated, and (*A*) then joined to the rest of the apparatus. The cup joint is sealed with a little mercury, a little also being poured into the funnel (*B*), so that the bore of the tap is quite filled. The stopcock (*c*) is opened, and connection made to a good pump until approximately a vacuum is established inside the apparatus. Entire freedom from air is not necessary, but when determining very small quantities of carbon dioxide (1 to 5 c.c. from 10 grams of soil), the pressure should be run down until the manometer indicates little more than the



vapour pressure of water within the apparatus. When dealing with larger quantities of gas, for example, 10 to 20 c.c., a mercury pump is not necessary, it is sufficient to use a good water pump or hand air pump that will establish an internal pressure of 50–60 mm. of mercury.

The stopcock (*d*) is closed, the height of the mercury in (*D*) and the temperature of the water-bath are read; this reading = *R*. Stopcock (*c*) is then closed, a well-boiled and cooled mixture of equal volumes of sulphuric acid and water is placed in the funnel (*B*), and a few c.c. introduced into the reacting bulb. Since it enters from below, the liquid and soil get well stirred up; the mixture is left for a few minutes

to cool down to the temperature of the bath, then the apparatus is shaken to expel the carbon dioxide present in excess in the solution, and allowed to stand, with further occasional shaking, until the gauge shows a constant reading.

The gas evolved causes an increase of pressure inside the apparatus, and the manometer column is read again  $= R_1$ . Communication is now made with the bulb (C) by opening the stopcock (c), the gas expands again into (C) and the mercury rises again in (D). A little time and shaking cause the gas dissolved in the liquid in (A) to come into equilibrium with the gas above at the new pressure; the manometer column is then read when constant, and  $= R_2$ .

Assuming the temperature,  $t$ , of the water-bath has remained constant, and calling  $d$  the difference in mm. between  $R$  and  $R_1$ ,  $d'$  the difference in mm. between  $R$  and  $R_2$ , and  $C$  the volume of the bulb (C), then the volume of gas evolved at N.T.P.  $= \frac{C.d.d'}{(d-d')760} \times$

$\frac{273}{273+t}$ . \* The operation amounts to finding an unknown volume of gas in (A) by the change in pressure produced when it expands by a known volume. The advantage of the method lies in the fact that the volume of soil, liquid, &c., which may have been introduced into (A) is immaterial, and does not appear in the calculation, and especially

\* The complete proof of the formula given is as follows :

Let  $x$  = the p. v. of the carbon dioxide evolved at the given temperature.  
 $A$  = the volume of the apparatus excluding (C) and the liquid in (A).  
 $C$  = the volume of (C).  
 $P$  = barometer reading.  
 $a$  = tension of aqueous vapour at the given temperature.  
 $k$  = the volume of carbon dioxide soluble in the liquid in (A) at unit pressure.

$R, R_1$  and  $R_2$  = the readings as above.

At starting, the apparatus contains some air  $= (A+B)(P-R-a)$ .  
 (C) is shut off and  $x$  of carbon dioxide evolved. Then :

$$x + A(P-R-a) = A(P-R_1-a) + k(R-R_1)$$

$$\frac{x}{R-R_1} = A+k \quad \dots \dots \dots [1]$$

The gas is then allowed to expand into (C), when

$$x + (A+C)(P-R-a) = (A+C)(P-R_2-a) + k(R-R_2)$$

$$\frac{x}{R-R_2} = A+C+k \quad \dots \dots \dots [2]$$

Combining [1] and [2]

$$\frac{x}{R-R_2} = \frac{C+x}{R-R_1}$$

$$\text{whence } x = \frac{C(R-R_1)(R-R_2)}{R_2-R_1} = \frac{C.d.d'}{d-d'} \text{ as above.}$$

that the effect of the gas remaining dissolved in the liquid in (*A*) is also eliminated. The liquid is saturated by the gas, so that the gas within and without the liquid is in equilibrium. When the volume is increased by opening the stopcock to (*C*), an amount of gas, proportional to the reduction in pressure, escapes from the liquid. In brief, the gas contained in the liquid of (*A*) obeys the same laws as the gas above the liquid, and the liquid becomes practically only a portion of the gas-filled space of (*A*).

It is necessary to have some solid particles like soil or glass beads in (*A*), otherwise the liquid becomes, and remains, obstinately supersaturated with carbon dioxide, nor can the excess be shaken out. This tendency to supersaturation forms the chief difficulty in working with the apparatus; the amount of substance taken should be such that the pressure of the carbon dioxide liberated does not exceed 100 or 150 mm., or the time required to obtain equilibrium becomes very great, and may even amount to 2 or 3 hours. The lower the pressure, or, in other words, the smaller the amount of carbonate present, the easier the determination is to carry out; the limit is fixed only by the accuracy with which the gauge can be read.

Appended are a few numbers obtained with the apparatus in the case of pure sodium carbonate and Iceland spar, the bulb (*A*) being half filled with glass beads :

Number.	Substance taken.	CO <sub>2</sub> at N.T.P. (calc.).	CO <sub>2</sub> at N.T.P. (found).
1	0.000624 gram Na <sub>2</sub> CO <sub>3</sub>	0.13 c.c.	0.15 c.c.
2	0.00125   "   "	0.26   "	0.26   "
3	0.0025   "   "	0.53   "	0.51   "
4	0.005   "   "	1.06   "	1.00   "
5	0.010   "   "	2.11   "	2.00   "
6	0.020   "   "	4.22   "	4.38   "
7	0.0503   "   CaCO <sub>3</sub>	11.26   "	11.18   "

The apparatus may be conveniently applied to any reaction involving the measurement of a gas evolved from a liquid.

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# XI.—*Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds.*

By GILBERT THOMAS MORGAN, D.Sc.

THE action of a diazonium salt on an aromatic amine gives rise to a diazoamine or an aminoazo-compound, according as the diazonium residue  $R \cdot N_2 \cdot$  remains attached to the aminic nitrogen or takes up its position in the aromatic nucleus.

The former mode of combination occurs with the primary monoamines of the benzene series, these bases yielding diazoamines. The mono-alkylated monoamines of the benzene series, on the other hand, exhibit a tendency to form azo-compounds; methylaniline, for example, when treated with diazobenzenesulphonic acid, yields a mixture of the diazoamino-compound,  $SO_3H \cdot C_6H_4 \cdot N_2 \cdot NMePh$ , and the isomeric aminoazo-acid,  $SO_3H \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NHMe$  (Bernthsen and Goske, *Ber.*, 1887, 20, 925, Bamberger and Wulz, *Ber.*, 1891, 24, 2082).

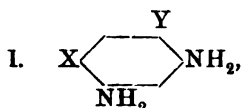
A somewhat heterogeneous class of bases including the following substances:—diphenylamine, the naphthylamines and their mono-alkyl derivatives, *m*-phenylenediamine and certain of its homologues and substitution products, gives rise to aminoazo-compounds without the intermediate formation of stable diazoamines. Dimethylaniline and a few other tertiary amines also yield aminoazo-derivatives, but with these bases the production of diazoamines is obviously impossible.

There is some reason for believing that the difference between the behaviour of aniline and that of *m*-phenylenediamine towards diazonium salts is due to the greater reactivity of the disubstituted ring, so that substituent radicles find their way more readily into the aromatic nucleus of the diamine than into that of the monoamine. The introduction of chlorine and bromine by the action of hypochlorous and hypobromous acids respectively is a case in point; the latter halogen enters the nucleus of the diamine so easily that *m*-phenylenediacetyldibromoamine,  $C_6H_4(NBrAc)_2$ , could not be isolated (Morgan, *Trans.*, 1900, 77, 1209; Chattaway and Orton, *Ber.*, 1901, 34, 160), whereas phenylacetyl bromoamine,  $Ph \cdot NBrAc$ , is a comparatively stable substance (Chattaway and Orton, *Trans.*, 1899, 75, 1046; 1900, 77, 800).

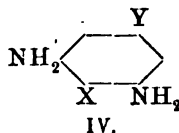
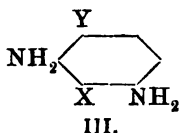
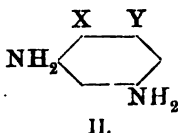
Reasoning by analogy, it seems probable that the initial phase of the interaction between *m*-phenylenediamine and a diazonium salt involves the formation of an unstable diazoamine, this substance immediately changing into the isomeric aminoazo-derivative. This assumption is, however, not supported at present by any direct experimental evidence. With the view of gaining additional information as

to the course of this reaction, the formation of azo-derivatives of the homologues and substitution products of *m*-phenylenediamine has been studied. 2:4-Tolylenediamine has long been known to be as reactive towards diazo-compounds as *m*-phenylenediamine itself, and more recently this was also shown to be true of 1-chloro-2:4-phenylenediamine and its bromine analogue. These bases readily yield azo-compounds, which, except for some slight differences in shade of colour, closely resemble those derived from the parent base. The hydrochlorides of chloro- and bromo-chrysoidines, for example, are obtained in crystals very similar in shape and colour to those of the ordinary chrysoidine of commerce.

The disubstituted *m*-diamines may be divided into two series with reference to their behaviour towards diazonium salts. The first series consists of the bases having the general formula

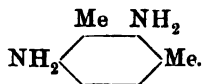
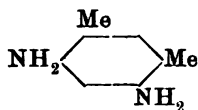


whilst the second comprises all those disubstituted *m*-diamines which contain one free para-ortho-position with respect to the amino-groups. The bases of the second series can be grouped together, because, providing this condition is fulfilled, the nature and position of the two substituent radicles exercise very little influence either on the course of the reaction or on the colour of the resulting azo-compound. An amine of this series may possess any one of the following formulæ :



Diamines corresponding with formulæ II and III have been investigated and the results compared with those obtained in the case of their isomerides belonging to series I.

The first diamines to be examined from this standpoint were the two diamino-*m*-xylenes described by Grevingk (*Ber.*, 1884, 17, 2426), these bases having the following constitutions :



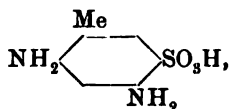
The former is produced by the reduction of 2:6-dinitro-*m*-xylene, the chief product of the nitration of *m*-xylene; whilst the latter is

obtained from 2:4-dinitro-*m*-xylene, this nitro-compound being a bye-product in the same operation.

Grevingk (*loc. cit.*) states that both these bases, when treated with benzenediazonium chloride, give colouring matters of the chrysoidine type, but he does not seem to have isolated any definite products. Witt, however, after an unsuccessful attempt to prepare an azo-compound by the action of diazobenzenesulphonic acid on the symmetrical base, maintains that this diamine does not yield chrysoidine derivatives (*Ber.*, 1888, 21, 2419).

As a matter of fact, the two isomerides behave very differently towards diazonium compounds. The consecutive base reacts just like 2:4-tolylenediamine, readily yielding a red azo-compound when treated with benzenediazonium chloride in the presence of sodium acetate; the symmetrical diamine, on the other hand, gives rise to a voluminous, brownish-yellow precipitate, which froths considerably, evolving nitrogen, and finally becomes resinous, even while in contact with the ice-cold mother liquor. This unpromising result was experienced with other symmetrically disubstituted *m*-diamines and seemed to confirm Witt's conclusion.

These failures could not, however, be accepted as conclusive evidence that the diamines of the type indicated by formula I cannot yield azo-compounds, inasmuch as the firm of Oehler & Co. has patented the production of colouring matters derived from 2:4-tolylenediamine-5-sulphonic acid (D.R.-P. 40905),



a substance having a constitution similar to that of the bases in question. Accordingly, further experiments were made with different diazo-compounds, until, finally, it was found that these bases would combine with primulin dyed and diazotised on the cotton fibre. Under these conditions, the symmetrically disubstituted diamines yielded azo-colouring matters possessing a yellowish-brown colour, and differing altogether from the reddish-brown compounds produced by similar means from the diamines belonging to the second series. These results show unmistakably that the relative position of the azo- and amino-groups is the most important factor in determining the shade of colour produced.

With the experience gained in these experiments on diazotised primulin, another attempt was made to prepare azo-compounds from 4:6-diamino-*m*-xylene and the simpler diazonium salts. The product of reaction was allowed to remain in the ice-cold solution for

one or two hours and the tarry precipitate then washed, dried, and carefully extracted with alcohol or benzene. In this way, a small yield of aminoazo-compound was produced and the reaction was shown to occur both with benzene- and *p*-toluene-diazonium salts.

The investigation was now extended to the symmetrical base, 5-chloro-2:4-tolylenediamine, simultaneously described by Reverdin and Crépieux (*Ber.*, 1900, 33, 2507) and by Morgan (*Trans.*, 1900, 77, 1209), and also to its isomeride, 2-chloro-3:5-tolylenediamine, prepared by Nietzki and Rebe (*Ber.*, 1892, 25, 3005). The latter compound contains one free para-ortho-position with respect to the amino-groups and might be expected to resemble 2:4-tolylenediamine and 2:4-diamino-*m*-xylene in its behaviour towards diazonium salts. This anticipation was completely confirmed; the interaction resulted in the immediate formation of an azo-compound, the yield being practically quantitative.

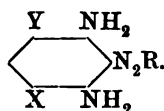
The symmetrical isomeride behaved like the similarly constituted 4:6-diamino-*m*-xylene; a brownish-yellow, voluminous precipitate was again produced, which evolved nitrogen and speedily became resinous. In this case, also, an azo-compound was extracted from the tarry product, but the yield was even poorer than that obtained in the experiment with the xylene base.

Since 4:6-dichloro-*m*-phenylenediamine (*Trans.*, 1900, 77, 1206) combines with diazotised primulin, an attempt was made to condense it with benzenediazonium chloride and its *p*-toluene homologue. In these experiments, there was a considerable amount of frothing and formation of resinous product, but the precipitate, on extraction, yielded a large amount of unaltered base and did not furnish any azo-compound. Although this result does not establish beyond doubt the fact that an azo-derivative is not produced, yet, in conjunction with the evidence obtained from the preceding experiments, it seems to indicate that, with these symmetrically disubstituted *m*-diamines, the tendency to form an azo-compound diminishes as the acidity of the molecule increases. This increase in acidic character results from the gradual replacement of methyl by chlorine, the pairs of substituent radicles in the three diamines being respectively 2Me, ClMe, and 2Cl.

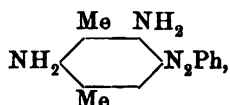
The brownish-yellow precipitates, which evolve nitrogen and become tarry, are probably unstable diazoamines. This conjecture receives additional support from the fact that under comparable conditions diaminomesitylene yields a similar, readily decomposable product, and in this instance the unstable substance cannot possibly be an azo-derivative. Meldola has also noticed the formation of a labile intermediate diazoamino-compound in the preparation of *p*-nitrobenzene-5-azo-4-*m*-xylidine (*Trans.*, 1883, 43, 428).

The aminoazo-bases derived from 4:6-diamino-*m*-xylene and 5-chloro-

2:4-tolylenediamine contain the azo-groups in the position contiguous to the two amino-radicles, their constitution being indicated by the general formula

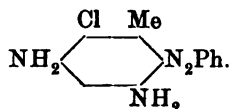


The azo-compound derived from 2:4-diamino-*m*-xylene has the constitution



since the position occupied by the azo-group is the only reactive position available in the original diamine.

In the case of 2-chloro-3:5-tolylenediamine, the azo-group may enter the ring in either the di-ortho-position or in one of the two para-ortho-positions with respect to the amino-radicles. The ease with which the azo-compound is produced in almost theoretical yield renders it in the highest degree probable that the entrant radicle takes up the para-ortho-position forming a colour base having the following configuration,



Moreover, the azo-compound produced on the cotton fibre from this diamine and diazotised primulin has the reddish-brown colour characteristic of the colouring matters having this constitution.

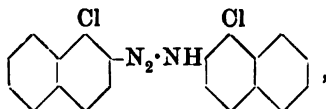
The naphthylamines and their derivatives containing hetero-nuclear substituents belong to the class of amines yielding azo-compounds without the intermediate formation of stable diazoamines, and are thus distinguished from aniline and its homologues, the only exception on record being  $\beta$ -naphthylamine-8-sulphonic acid, which, unlike its isomerides, gives a stable diazoamino-compound with benzenediazonium chloride (Witt, *Ber.*, 1888, 21, 3483).

A similar difference has been noticed in the behaviour of the two series of amines towards formaldehyde,  $\beta$ -naphthylamine yielding derivatives containing the methylene carbon atom attached to the aromatic nuclei (Trans., 1898, 73, 536), whereas aniline and its homologues give rise to intermediate compounds of the methylenedianiline and methylenedianiline types, containing methylene united with the nitrogen of one or two amino-groups. The investigation of these methylene compounds (Morgan, Trans., 1900, 77, 814) also showed

that the presence of a substituent radicle in the  $\alpha$ -position contiguous to the amino-radicle of  $\beta$ -naphthylamine prevented the transference of methylene into the ring.

Inasmuch as in their reactions with aromatic amines, formaldehyde and diazonium salts attack similar positions in the basic molecule it might be expected that a  $\beta$ -naphthylamine derivative substituted in the manner indicated would yield a diazoamine but not an azo-compound.

One compound of this type, namely, 2-diazoamino-1-chloro-4-bromonaphthalene, has already been obtained by Meldola and Streatfeild (*Trans.*, 1895, 67, 911) by the action of nitrous acid on 1-chloro-4-bromo- $\beta$ -naphthylamine. If the production of this diazoamine is determined by the presence of the chlorine atom in the  $\alpha$ -position contiguous to the amino-radicle, then it should be possible to obtain similar compounds from 1-chloro- $\beta$ -naphthylamine. The experimental results amply confirmed this assumption. The action of nitrous acid (1 mol.) on this amine (2 mols.) gave rise to 2-diazoamino-1-chloronaphthalene,



a well defined diazoamine resembling the compound described by Meldola and Streatfeild.

Mixed diazomines also were produced by the interaction of various diazonium salts and 1-chloro- $\beta$ -naphthylamine. *p*-Nitrobenzene-2-diazoamino-1-chloronaphthalene, prepared by the action of *p*-nitrobenzenediazonium chloride on this base, was also produced by the condensation of 1-chloro-2-naphthalenediazonium chloride on *p*-nitroaniline; this result indicates that Kekulé's rule relating to the formation of mixed diazoamines is applicable to those containing both naphthalene and benzene nuclei.

These diazoamines do not show any tendency to change into amino-azo-compounds containing the azo-group attached to the naphthalene nucleus. Here also, as in the case of the methylene derivatives, the directing influence of the amino-radicle in  $\beta$ -naphthylamine seems to be exerted only in one direction, and accordingly the substituent radicles readily shift into the contiguous  $\alpha$ -position, but do not replace the hydrogen attached to the adjacent  $\beta$ -carbon atom.

## EXPERIMENTAL.

*Action of Diazonium Salts on the m-Diamino-m-xylenes.*

*Preparation of the Diamines.*—*m*-Xylene is nitrated in quantities of 250 grams by slowly adding a well-cooled mixture of concentrated nitric and sulphuric acids (2·3 parts  $\text{HNO}_3$  of sp. gr. 1·52 to 2 parts  $\text{H}_2\text{SO}_4$ ) to the hydrocarbon surrounded by ice and salt. When the hydrocarbon is added to the acid, a considerable amount of trinitro-xylene is formed at the commencement of the operation. The mixture, after remaining for several hours at the ordinary temperature, is warmed for two hours at 40–50° and then poured on to ice. The crude, viscid nitro-compounds are drained from oily products and the solid residue is crystallised from alcohol, the last operation being repeated two or three times. The crystals obtained in this manner consist of 4:6-dinitro-*m*-xylene melting at 91–92° (Grevingk, *loc. cit.*, gives m. p. 93°). The alcoholic mother liquors, when united and allowed to evaporate spontaneously, deposit an oily substance which is withdrawn as soon as the separation of crystalline product commences. This second crop of solid nitro-compound is crystallised repeatedly from alcohol, and the final product consists, very largely, of 2:4-dinitro-*m*-xylene, crystallising in rosettes of hard, well-defined, flattened needles which melt somewhat indefinitely at 58–61°. Grevingk gives 80° as the melting point of the pure compound. As repeated crystallisation does not raise the melting point, the substance is reduced without further purification. The alcoholic mother liquors obtained by working up 1250 grams of *m*-xylene yield about 120 grams of the partially purified nitro-compound. The final mother liquors furnish a further quantity of oily nitro-compound. These oily products, obtained at various stages of the operation, when united and reduced give rise to impure 4:6-diamino-*m*-xylene.

The diamines are obtained by reducing the respective dinitro-xylenes with iron, 100 grams of the nitro-compound being treated with 130 grams of iron filings, 800 c.c. of water, and 12 c.c. of concentrated hydrochloric acid. The whole of the water is not added at the commencement of the operation, but about 300 c.c. are introduced gradually during the reduction in order to moderate the reaction, which sometimes becomes very violent. The product, rendered alkaline with 8 grams of sodium hydrogen carbonate, is filtered from iron oxide; the filtrate acidified with acetic acid is treated with excess of acetic anhydride (about 60 grams). The precipitated diacetyl derivative is collected after 12 hours; the filtrate, when concentrated and treated with a further quantity of the anhydride, yields a second crop of diacetyldiaminoxylene. After crystallisation from glacial acetic acid,

the diacetyl compound is hydrolysed with concentrated hydrochloric acid and the resulting diaminoxylene hydrochloride crystallised from water and then decomposed with the calculated amount of concentrated potassium hydroxide solution.

The 4 : 6-diamino-*m*-xylene separates in the solid form and is finally purified by crystallisation from water ; it then melts at  $104^{\circ}$ , the melting point being identical with that given by Grevingk. The isomeric 2 : 4-diamino-*m*-xylene separates as an oil ; this, after separation from the potassium chloride solution by means of ether, is distilled under diminished pressure. After three distillations, a viscoid oil is obtained boiling at  $170$ — $174^{\circ}$  under 13 mm. pressure ; this substance, when cooled to  $-10^{\circ}$ , gradually solidifies to a mass of crystals melting indefinitely at about  $17^{\circ}$ . The yield from 1250 grams of xylene is about 25 grams.

These bases have been characterised by means of their acyl derivatives, as these latter are well defined substances easily prepared by the ordinary processes.

*Diformyl-4 : 6-diamino-m-xylene* crystallises from water in colourless, slender, flattened, silky needles and melts at  $182$ — $183^{\circ}$ .

0.2122 gave 27.1 c.c. moist nitrogen at  $18^{\circ}$  and 758 mm.  $N = 14.71$ .  
 $C_{10}H_{12}O_2N_2$  requires  $N = 14.58$  per cent.

The *diacetyl* derivative is very sparingly soluble in alcohol, but dissolves more readily in glacial acetic acid ; it crystallises in lustrous, silky needles and melts above  $260^{\circ}$ .

The *dibenzoyl* derivative,  $C_6H_5Me_2(NH \cdot CO \cdot C_6H_5)_2$ , crystallises from alcohol or ethyl acetate in small, lustrous plates and melts at  $252$ — $253^{\circ}$ .

0.1570 gave 11.5 c.c. moist nitrogen at  $18^{\circ}$  and 758 mm.  $N = 8.43$ .  
 $C_{22}H_{20}O_2N_2$  requires  $N = 8.13$  per cent.

*Diformyl-2 : 4-diamino-m-xylene* crystallises from water, alcohol, or ethyl acetate in rosettes of colourless needles and melts at  $219$ — $220^{\circ}$ .

0.1148 gave 14.4 c.c. moist nitrogen at  $19^{\circ}$  and 759 mm.  $N = 14.29$ .  
 $C_{10}H_{12}O_2N_2$  requires  $N = 14.58$  per cent.

The *diacetyl* derivative is sparingly soluble in alcohol and crystallises from glacial acetic acid in colourless, felted needles ; it melts above  $260^{\circ}$ .

The *dibenzoyl* derivative crystallises from alcohol in felted needles and melts at  $232^{\circ}$ .

0.1458 gave 10.8 c.c. moist nitrogen at  $18^{\circ}$  and 759 mm.  $N = 8.56$ .  
 $C_{22}H_{20}O_2N_2$  requires  $N = 8.13$  per cent.



*Action of Benzenediazonium Chloride on 2:4-Diamino-m-xylene.*

—A solution of benzenediazonium chloride, prepared from 5.4 grams of aniline hydrochloride, is added to a dilute ice-cold solution of 5 grams of the diamine acidified with 3 c.c. of concentrated hydrochloric acid. The solution remains clear until excess of crystallised sodium acetate (10 grams) is added and then a gelatinous red precipitate is produced which after remaining for a few hours is collected. The substance is purified by crystallisation from methyl alcohol.

*Benzene-5-azo-2:4-diamino-m-xylene* crystallises in yellowish-brown needles and melts at 208—209°.

0.0308 gave 6.2 c.c. moist nitrogen at 18° and 769 mm.  $N = 23.54$ .

$C_{14}H_{16}N_4$  requires  $N = 23.33$  per cent.

The azo-compound is distinctly basic and dissolves in dilute hydrochloric acid; the hydrochloride, however, is amorphous and separates in masses of red filaments. The platinichloride is a brick-red, amorphous, insoluble salt.

*Benzene-5-azo-2:4-diacetyldiamino-m-xylene,*



prepared by warming the crude azo-base for a few minutes with a mixture of glacial acetic acid and acetic anhydride, crystallises from alcohol in orange plates melting above 260°.

0.1952 gave 28.8 c.c. moist nitrogen at 19° and 769 mm.  $N = 17.16$ .

$C_{18}H_{20}O_2N_4$  requires  $N = 17.28$  per cent.

A comparative experiment made with 2:4-tolylenediamine shows that the two bases behave in a precisely similar manner towards diazonium salts.

*Benzene-5-azo-2:4-tolylenediamine* (compare Stebbins, *Ber.*, 1880, 13, 717) crystallises in orange-brown needles or leaflets and melts at 161°.

*Benzene-5-azo-2:4-diacetyltolylenediamine,*



crystallises in flattened, orange prisms and melts at 216—217°.

0.1756 gave 27.4 c.c. moist nitrogen at 20° and 769 mm.  $N = 18.06$ .

$C_{17}H_{18}O_2N_4$  requires  $N = 18.06$  per cent.

*Action of Diazonium Salts on 4:6-Diamino-m-xylene.*—The same proportions of diamine and benzenediazonium chloride are employed as in the preceding experiment. On adding the sodium acetate to the clear solution containing the other reagents, a bulky, brownish-yellow precipitate is formed which rapidly darkens and becomes resinous. After 2 hours, the product is collected, washed, dried, and extracted with alcohol. From this extract, *benzene-5-azo-4:6-diamino-m-*

*xylene*,  $C_6H_5 \cdot N_2 \cdot C_6HMe_2(NH_2)_2$ , separates in deep red, rhombic plates which after two crystallisations melt at  $182-183^\circ$ . The compound is not decomposed on long boiling with alcoholic hydrochloric acid. It develops a deep orange coloration with concentrated sulphuric acid, and readily yields acyl derivatives by the ordinary processes.

0.0832 gave 0.2140  $CO_2$  and 0.0503  $H_2O$ .  $C = 70.14$ ;  $H = 6.70$ .

0.1030 „ 20.3 c.c. moist nitrogen at  $18^\circ$  and 767 mm.  $N = 22.98$ .

$C_{14}H_{16}N_4$  requires  $C = 70.0$ ;  $H = 6.66$ ;  $N = 23.30$  per cent.

The *diacetyl* derivative,  $C_6H_5 \cdot N_2 \cdot C_6HMe_2(NH \cdot CO \cdot CH_3)_2$ , obtained from the preceding base by the action of acetic anhydride, crystallises from alcohol in brownish-red needles and melts above  $260^\circ$ .

0.1390 gave 20.8 c.c. moist nitrogen at  $18^\circ$  and 759 mm.  $N = 17.10$ .

$C_{18}H_{20}O_2N_4$  requires  $N = 17.28$  per cent.

*p-Toluene-5-azo-4:6-diamino-m-xylene*,  $C_6H_4Me \cdot N_2 \cdot C_6HMe_2(NH_2)_2$ , obtained by substituting an equivalent amount of *p*-toluidine for the aniline employed in the preparation of the preceding azo-diamine, crystallises from alcohol or benzene in deep red, rhombic plates and melts at  $165-166^\circ$ . It closely resembles its homologue in chemical and physical properties.

0.1817 gave 34.5 c.c. moist nitrogen at  $21^\circ$  and 754 mm.  $N = 21.43$ .

$C_{15}H_{18}N_4$  requires  $N = 22.04$  per cent.

*Action of Diazonium Salts on 5-Chloro-2:4-tolylenediamine and  
2-Chloro-3:5-tolylenediamine.*

5-Chloro-2:4-tolylenediamine can be readily obtained in large quantities by the author's method (Trans., 1900, 77, 1209), and it has been further characterised by the preparation of a series of its diacyl derivatives.

*Diformyl-5-chloro-2:4-tolylenediamine*,  $C_6H_2MeCl(NH \cdot CHO)_2$ , prepared by heating the base for 3 hours with 2—3 parts of concentrated formic acid, is obtained as a dark brown precipitate on treating the product with dilute ammonia; it is purified by three crystallisations from water in the presence of animal charcoal, and finally separates from this solvent in colourless, silky needles melting at  $166^\circ$ .

0.1218 gave 0.2370  $CO_2$  and 0.0520  $H_2O$ .  $C = 51.72$ ;  $H = 4.74$ .

0.2076 „ 24 c.c. moist nitrogen at  $18^\circ$  and 768 mm.  $N = 13.49$ .

0.1318 „ 0.0869  $AgCl$ .  $Cl = 16.31$ .

$C_9H_9ON_2Cl$  requires  $C = 50.82$ ;  $H = 4.23$ ;  $N = 13.18$ ;  $Cl = 16.70$  per cent.

The diacetyl derivative melts above  $260^\circ$ , and not at  $240^\circ$  as previously indicated; it is obtained free from the monoacetyl compound

by heating the base with excess of acetic anhydride, and crystallising the product from glacial acetic acid; it is sparingly soluble in methyl, ethyl, or amyl alcohol, separating from any of these solvents as a microcrystalline powder; it crystallises from pyridine or acetic acid in small prisms.

0.1405 gave 0.0842 AgCl.  $\text{Cl} = 14.83$ .

$\text{C}_{10}\text{H}_{13}\text{ON}_2\text{Cl}$  requires  $\text{Cl} = 14.76$  per cent.

The *dibenzoyl* derivative, prepared by the Schotten-Baumann method, crystallises from alcohol in colourless, acicular lamellæ and melts at  $205^\circ$ .

0.2209 gave 0.0890 AgCl.  $\text{Cl} = 9.96$ .

0.1576 „ 10.5 c.c. moist nitrogen at  $19^\circ$  and 761 mm.  $\text{N} = 7.70$ .

$\text{C}_{21}\text{H}_{17}\text{ON}_2\text{Cl}$  requires  $\text{Cl} = 9.74$ ;  $\text{N} = 7.68$  per cent.

*Benzene-3-azo-5-chloro-2:4-tolylenediamine*,  $\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_6\text{HClMe}(\text{NH}_2)_2$ .—The brownish-yellow precipitate produced by adding an excess of sodium acetate to a dilute hydrochloric acid solution containing equivalent quantities of benzenediazonium chloride and 5-chloro-2:4-tolylenediamine, is allowed to remain in contact with the mother liquor for 2 hours and then collected, dried, and extracted with alcohol. The filtered extract slowly deposits a crop of dark brown crystals contaminated with tar; the crude *benzene-3-azo-5-chloro-2:4-tolylenediamine* is repeatedly crystallised from alcohol and finally obtained in dark brownish-red plates melting at  $147^\circ$ . The compound is not decomposed by prolonged boiling with alcoholic hydrochloric acid and develops a deep yellowish-brown coloration with concentrated sulphuric acid; it readily yields acyl derivatives when treated with the appropriate reagents.

The *dibenzoyl* derivative,  $\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_6\text{HMeCl}(\text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5)_2$ , produced by the Schotten-Baumann method, crystallises from alcohol in transparent, brownish-yellow plates and melts at  $236\text{--}237^\circ$ .

0.1692 gave 17.3 c.c. moist nitrogen at  $19^\circ$  and 765 mm.  $\text{N} = 11.83$ .

$\text{C}_{27}\text{H}_{21}\text{O}_2\text{N}_4\text{Cl}$  requires  $\text{N} = 11.95$  per cent.

The *acetyl* derivative crystallises from alcohol in brownish-red, flattened prisms, and melts at  $225^\circ$ .

*p-Toluene-3-azo-5-chloro-2:4-tolylenediamine*,

$\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{HClMe}(\text{NH}_2)_2$ .

—This azo-compound closely resembles its lower homologue and is prepared in a precisely similar manner. In this case also there a considerable evolution of nitrogen accompanied by the formation of much tarry product, and the yield of crystalline base is small. The substance crystallises from alcohol in dark brown plates and melts at  $152^\circ$ .

0.1196 gave 0.0600 AgCl. Cl = 12.41.

0.1971 „ 35.2 c.c. moist nitrogen at 21° and 754 mm. N = 20.16.

$C_{14}H_{15}N_4Cl$  requires Cl = 12.93; N = 20.00 per cent.

A dilute hydrochloric acid solution of 4:6-dichloro-*m*-phenylenediamine and benzenediazonium chloride, when treated with sodium acetate, yields a yellow precipitate, which, when crystallised from alcohol, separates in brown leaflets melting at 137°. The product contains from 37 to 39.6 per cent. of chlorine and seems to consist chiefly of unchanged diamine; this base melts at 137° and contains 40.11 per cent. of chlorine, whereas the percentage of this element in the required azo-compound would be 25.26. A negative result was also obtained with *p*-toluenediazonium chloride; in this experiment, 14.7 grams of the diamine were employed, and 8.7 grams of the unchanged base were recovered after recrystallisation, the other products of reaction being tarry and indefinite.

On the other hand, the dichlorodiamine combines with diazotised primulin, for a piece of cotton cloth impregnated with this diazo-compound and placed in an aqueous solution of the base gradually acquires a brownish-orange colour, similar in shade to the azo-colouring matters produced under these conditions from 5-chloro-2:4-tolylene-diamine and 4:6-diamino-*m*-xylene.

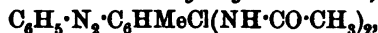
*Benzene-6-azo-2-chloro-3:5-tolylenediamine*.—2-Chloro-3:5-tolylenediamine (*Ber.*, 1892, 25, 3005), is readily obtained from 3:5-dinitro-2-chlorotoluene, the nitration product of *o*-chlorotoluene, by the iron-filings method of reduction. The iron oxide is freed from the diamine by washing with alcohol; the alcoholic and aqueous extracts are mixed together, acidified with acetic acid, and treated with excess of acetic anhydride. The acetyl derivative, crystallised from glacial acetic acid, is hydrolysed with hydrochloric acid, and the free base purified by crystallisation from water, in which solvent it is more soluble than its symmetrical isomeride; it separates in long needles melting at 74°.

The azo-compound, prepared in the ordinary way, separates immediately as a flocculent, yellow precipitate on the addition of sodium acetate to the hydrochloric acid solution of its generators; it crystallises from a mixture of benzene and petroleum in tufts of long, orange-red, acicular prisms, these crystals being sometimes more than an inch in length. The substance melts at 134°, yields a deep brownish-red coloration with concentrated sulphuric acid, and is not decomposed by prolonged boiling with alcoholic hydrochloric acid.

0.1448 gave 26.2 c.c. moist nitrogen at 18° and 766 mm. N = 21.00.

0.1643 „ 0.0928 AgCl. Cl = 13.97.

$C_{12}H_{13}N_4Cl$  requires Cl = 13.62; N = 21.49 per cent.

*Benzene-6-azo-2-chloro-3 : 5-diacetyltolylenediamine,*

produced by gently heating the azo-base with acetic anhydride, is readily soluble in acetic acid or benzene, but dissolves only sparingly in alcohol or ethyl acetate; it crystallises in silky, orange needles and melts at 251°.

0·1074 gave 14·6 c.c. moist nitrogen at 17° and 762 mm. N = 15·68.

0·1631 „ 0·0663 AgCl. Cl = 10·06.

$\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}_4\text{Cl}$  requires Cl = 10·30; N = 16·25 per cent.

The *dibenzoyl* derivative obtained by the Schotten-Baumann method crystallises from benzene in orange needles and melts at 233°.

0·1162 gave 11·7 c.c. moist nitrogen at 18° and 758 mm. N = 11·69.

0·0717 „ 0·0213 AgCl. Cl = 7·35.

$\text{C}_{27}\text{H}_{21}\text{O}_2\text{N}_4\text{Cl}$  requires Cl = 7·58; N = 11·95 per cent.

*Action of Diazonium Salts on 1-Chloro-β-naphthylamine.*

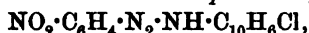
*2-Diazoamino-1-chloronaphthalene*,  $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\text{Cl}$ , separates as a light yellow precipitate on adding excess of sodium acetate to the mixture formed by slowly dropping a glacial acetic acid solution of 1-chloro-β-naphthylamine (1 mol.) into a hydrochloric acid solution of 1-chloro-2-naphthalenediazonium chloride (1 mol.); it crystallises from benzene or chloroform in golden-yellow needles and melts at 152°. The diazoamine may also be produced by adding sodium nitrite (1 mol.) to an ice-cold alcoholic solution of 1-chloro-β-naphthylamine (2 mols.) acidified with hydrochloric acid, the precipitation of the compound being completed by the addition of a saturated aqueous solution of sodium acetate. The product obtained in this way is, however, often contaminated with an amorphous, red substance, which is not readily removed in the subsequent crystallisations.

0·1711 gave 17·1 c.c. moist nitrogen at 21·5° and 769 mm. N = 11·49.

0·2358 „ 0·1817 AgCl. Cl = 19·19.

$\text{C}_{20}\text{H}_{13}\text{N}_3\text{Cl}_2$  requires Cl = 19·39; N = 11·47 per cent.

Although insoluble in alcohol, it readily dissolves in alcoholic potassium hydroxide, yielding a deep orange-coloured solution, this result pointing to the existence of a potassium derivative. The compound is remarkably sensitive to light, and after a few weeks' exposure its crystals, although retaining their shape, acquire a dark chocolate colour; it is decomposed on warming with hydrochloric acid, evolving nitrogen and yielding 1-chloro-β-naphthylamine and resinous products.

*p*-Nitrobenzene-2-diazoamino-1-chloronaphthalene,

is obtained by adding a hydrochloric acid solution of *p*-nitrodiazonium chloride (prepared from 3 grams of *p*-nitroaniline) to a cooled alcoholic solution of 1-chloro- $\beta$ -naphthylamine (4 grams), the precipitation of the diazoamine being completed by the addition of sodium acetate. It may also be prepared by mixing together solutions containing equivalent quantities of 1-chloro-2-naphthalenediazonium chloride and *p*-nitroaniline. The diazoamine produced by either of these processes is obtained as a voluminous, yellow precipitate; it is almost insoluble in alcohol and only sparingly soluble in benzene, separating from the latter solvent in brownish-yellow leaflets melting and decomposing at 197—198°.

0.1342 gave 19.8 c.c. moist nitrogen at 21° and 759 mm. N = 17.08.

0.1614 „ 0.0692 AgCl. Cl = 10.65.

$\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_4\text{Cl}$  requires Cl = 10.87; N = 17.15 per cent.

The diazoamine is fairly soluble in hot chloroform, but when boiled for some time with this solvent it partly decomposes. It is acidic in character and its potassium derivative, produced by dissolving the compound in an alcoholic solution of potassium hydroxide, yields a deep purple solution.

*Ethyl Derivative of p*-Nitrobenzene-2-diazoamino-1-chloronaphthalene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{NEt} \cdot \text{C}_{10}\text{H}_6\text{Cl}$ .—An alcoholic solution of the potassium derivative of the preceding diazoamine is boiled with a slight excess of ethyl iodide until the deep purple coloration of the mixture changes to orange. The crystalline product obtained on cooling the alcoholic solution is purified by crystallisation from benzene, and separates from this solvent in hard, orange-yellow, prismatic crystals melting at 193—194°. This compound does not develop a purple coloration with alcoholic potassium hydroxide and on analysis gives numbers corresponding with those required for an *ethyl* derivative of the mixed diazoamine.

0.2382 gave 32.1 c.c. moist nitrogen at 19° and 769 mm. N = 15.68.

0.1452 „ 0.0584 AgCl. Cl = 9.96.

$\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}_4\text{Cl}$  requires Cl = 10.01; N = 15.80 per cent.

A diazoamine resembling the preceding ethyl compound, but melting at 182—183°, is produced by adding a solution of 1-chloro-2-naphthalenediazonium chloride to an alcoholic solution of ethyl-*p*-nitroaniline. The study of these alkyl derivatives of naphthalenoid diazoamines is, however, still incomplete owing to the difficulty experienced in alkylating 1-chloro- $\beta$ -naphthylamine and its analogues.

My best thanks are due to Miss F. M. G. Micklethwait for assisting in the preparation and analysis of several of the compounds described in this communication, and to Mr. E. Lodge for examining the tinctorial properties of the two series of aminoazo-derivatives.

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## XII.—*Cyanohydroxypyridine Derivatives from Diacetonitrile. New Derivatives of $\psi$ -Lutidostyryl.*

By JAMES MOIR, M.A., B.Sc., 1851 Exhibition Scholar of Aberdeen University.

DIACETONITRILE was first prepared in 1889 by R. Holtzwardt, in E. von Meyer's laboratory, by the action of sodium on acetonitrile in the presence of a diluent such as ether, which serves to keep the temperature below that required to form the termolecular polymeride cyanmethine (*J. pr. Chem.*, 1889, **39**, [ii], 329).

While attempting to make the latter compound for another purpose, I found that even if acetonitrile alone be used, *diacetonitrile* is almost the sole organic product (instead of cyanmethine) if the sodium be present in excess. During these experiments, in attempting to crystallise the diacetonitrile from hot water, I noticed that ammonia was evolved during the digestion of the solution on the water-bath, and that subsequently a different substance crystallised from the liquid.

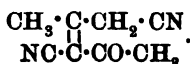
The formation of this substance, which is sparingly soluble in all the ordinary solvents and beautifully crystalline, had already been observed by Holtzwardt, who made an extensive study of diacetonitrile. Although he analysed the compound and assigned to it the formula  $C_8H_8ON_2$ , unfortunately he did not succeed in elucidating its constitution. The mechanism of the process by which it arises is, however, not difficult to imagine, if it be remembered that, as Holtzwardt has shown, diacetonitrile has the constitution  $CH_3 \cdot C(NH_2) : CH \cdot CN$ , and that it is easily converted by hydrolysis into the isodynamic form of cyanacetone,  $CH_3 \cdot C(OH) : CH \cdot CN$ . If two molecules of the latter compound lose one of water, a compound of the formula  $C_8H_8ON_2$  will be produced. This formula is that of an anhydride of cyanacetone ;



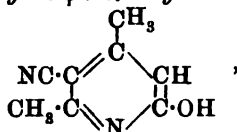
Holtzwardt therefore proposed to write the formula



von Meyer subsequently suggested the alternative formula



My experiments have led me to conclude that such formulæ afford no adequate explanation of the extreme stability and inactivity of the substance, and they seem to me to justify the conclusion that the compound is in reality 3-cyano-*ψ*-lutidostyryl:



or, more probably, a polymeride of that substance formed by a process analogous to that by which benzonitrile is converted into cyanphenine. Attempts to determine the molecular weight were frustrated by the insolubility of the substance.

In preparing diacetonitrile and the compound under discussion, the methods described by Holtzwardt and by von Meyer were in the main followed. As diluents of the acetonitrile, dry ether, benzene, and toluene were tried without much benefit. In all cases, the yield of diacetonitrile leaves much to be desired. The best results are obtained as follows. Forty grams of acetonitrile (distilled over phosphoric oxide or solid potash) having been covered with a layer of dry light petroleum (to exclude air), 10 grams of sodium in thickish slices are introduced gradually through the condenser. The action is very violent until the surface of the metal becomes coated; finally, the flask is heated during four hours on the water-bath. The mixture, having been transferred to a Buchner funnel, is thoroughly stirred, to separate the product from the sodium, which can then be mechanically removed. The solid—a mixture of sodium diacetonitrile with sodium cyanide—is mixed with just enough water to dissolve it; diacetonitrile separates as an oil and may be completely recovered by extracting with benzene and then evaporating off the solvent.

To prepare Holtzwardt's compound, the benzene extracts are digested with about 20 parts of water: as the benzene evaporates, ammonia is given off and the liquid becomes brown; eventually it deposits needles of the condensation compound. The mother liquor, on digestion with water, yields a further quantity together with a red gum. The product is obtained practically pure by one crystallisation from glacial acetic acid. The loss caused by the formation of bye-products in this double condensation is so great that the yield of the final product is seldom over 8 per cent. of the acetonitrile used.

The substance so obtained agrees on the whole with Holtzwardt's description, forming bundles of small, short needles; it has an intensely bitter taste. It is equally soluble in boiling water and alcohol to the extent of about 1 per cent.; it is more soluble in boiling glacial acetic acid, but in boiling benzene only to the extent of 1



part in 600. It crystallises out easily on cooling these solutions. I have to add the correction that the purified substance melts sharply at  $293^{\circ}$  ( $305^{\circ}$  corr.), although it darkens somewhat above  $280^{\circ}$ . It can be sublimed without much loss at a higher temperature. Holtzwardt states that his compound melted "oberhalb  $230^{\circ}$ "—a serious underestimate, as I have never observed a lower melting point than  $260^{\circ}$ , even in the case of the crude preparation. Holtzwardt's formula was confirmed by the following analysis:

0.1513 gave 0.3596  $\text{CO}_2$  and 0.0752  $\text{H}_2\text{O}$ .  $\text{C} = 64.82$ ;  $\text{H} = 5.52$ .

0.0855 ,, 13.7 c.c. moist nitrogen at  $13.5^{\circ}$  and 750 mm.  $\text{N} = 18.63$ .

$\text{C}_8\text{H}_8\text{ON}_2$  requires  $\text{C} = 64.79$ ;  $\text{H} = 5.45$ ;  $\text{N} = 18.95$  per cent.

Despite the presence of two nitrogen atoms, the compound is not basic and may be crystallised from aqueous acids; it does not combine with platinum chloride.

It is easily soluble in alkali hydroxides, metallic derivatives being formed; these can be isolated by adding excess of alkali, and crystallise well from a mixture of absolute alcohol and ether, although very soluble in spirit or acetone. The potassium derivative forms long, lustrous needles; the sodium derivative, short, opaque needles. That they are phenolic in character is shown by the fact that the addition of carbon dioxide or of ammonium salts to their solutions causes a precipitate of the original substance. Attempts were made to analyse these, but the results were vitiated by the rapid absorption of carbon dioxide during the drying; the figures are too low in consequence.

0.2472 potassium derivative gave 0.1100  $\text{K}_2\text{SO}_4$ .  $\text{K} = 19.97$ .

$\text{C}_8\text{H}_7\text{ON}_2\text{K}$  requires  $\text{K} = 21.01$  per cent.

0.4923 sodium derivative gave 0.1804  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 11.88$ .

0.1329 ,, ,, dried in a vacuum, gave 19.7 c.c. moist nitrogen at  $13^{\circ}$  and 746 mm.  $\text{N} = 17.2$ .

$\text{C}_8\text{H}_7\text{ON}_2\text{Na}$  requires  $\text{N} = 16.47$ ;  $\text{Na} = 13.54$  per cent.

Holtzwardt's compound is a substance of unusual stability, and is not affected by

- (1) Prolonged boiling with a 10 per cent. aqueous or alcoholic solution of sodium hydroxide.
- (2) Prolonged boiling with methyl iodide and sodium hydroxide.
- (3) Prolonged heating at  $120^{\circ}$  with 70 per cent. sulphuric acid.
- (4) Heating at  $80^{\circ}$  with fuming sulphuric acid.
- (5) Prolonged boiling with acetic anhydride.

It had previously been shown by workers in von Meyer's laboratory that it is not affected by acetyl chloride, hydroxylamine, nitrous acid, &c. It gives no coloration with nitrososulphuric acid. It is only slightly attacked by boiling dilute nitric acid and by permanganate,

and although it at once reduces a solution of chromium trioxide in acetic acid, nothing definite can be isolated. It is also scarcely affected by boiling its solution in absolute alcohol with a large excess of sodium.

The first clue to the nature of the substance was obtained by heating it with zinc dust; a distillate smelling like pyridine was obtained, but in too small a quantity for investigation.

The only attempt to hydrolyse the compound which has succeeded was performed by heating it with concentrated hydrobromic acid (*d* 1.47) in a sealed tube during 6 hours at 170°. A large yield of a substance was obtained, which proved to be  $\psi$ -lutidostyryl, or 2:4-dimethyl-6-hydroxypyridine, a substance first described by Hantzsch (*Ber.*, 1884, 17, 2904), derivatives of which have frequently been obtained by the interaction of ethyl acetoacetate or its derivatives and ammonia (*Gazzetta*, 1886, 16, 449; *Annalen*, 1890, 259, 169; *Trans.*, 1895, 67, 220; 1897, 71, 299, &c.).

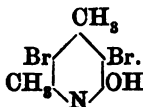
It will be seen that the formula of  $\psi$ -lutidostyryl,  $C_7H_9ON$ , may be derived from that of the original substance,  $C_8H_8ON_2$ , by displacing ON by H, and that the latter may be regarded as a cyano- $\psi$ -lutidostyryl. This was confirmed by the detection of carbon dioxide and ammonia as bye-products of the interaction, which may be expressed as follows:  $C_6HN(CH_3)_2(OH) \cdot CN + 2H_2O + HBr = C_6H_5N(CH_3)_2 \cdot OH + NH_4Br + CO_2$ . The slightly charred contents of the tube were extracted with water, filtered, and concentrated on the water-bath until the excess of acid was removed. On redissolving in a little water and adding soda until neutral, ammonia was freely evolved and the solution nearly solidified owing to the separation of a mass of long needles. These were filtered off and were found to be free from sodium and to melt at 171–173°. When heated in a test-tube, this product sublimed unchanged, the sublimate melting at 176°, and after recrystallisation at 177–178° (179–180° corr.). It boiled at 303° (uncorr.). On adding excess of sodium hydroxide to its concentrated solution, a sodium derivative crystallised out in thin, lustrous plates. The substance is therefore Hantzsch's  $\psi$ -lutidostyryl.

This was further established by directly comparing the product with a specimen made by Collie's method (*Trans.*, 1897, 71, 299). On bromination, it gave a product agreeing with Kerp's 3:5-dibromo- $\psi$ -lutidostyryl, but melting and decomposing at 253° (corr.) (Kerp gives 235°).

0.1058 gave 0.1405 AgBr. Br = 56.49.

$C_7H_9ONBr_2$  requires Br = 56.89 per cent.

This substance is therefore



On nitrating the  $\psi$ -lutidostyryl, two compounds were obtained, one of which was Collie's 5-nitro-derivative melting at  $254^\circ$  (corr.) ; the other which crystallised in rosettes of short needles melting constantly at  $196^\circ$  (corr.), also gave numbers on analysis agreeing with those required for a mononitro-compound, and was apparently a mixture of Collie's 5-nitro-compound with the 3-nitro-compound (m. p.  $260^\circ$  corr.), which I have obtained in a different way (see p. 116). The sodium derivative of the product melting at  $196^\circ$  (corr.) was made, washed with ether, and analysed :

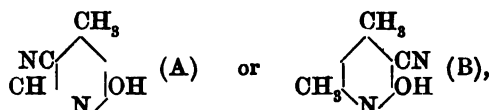
0.0650 gave 0.0234  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 11.68$ .

$\text{C}_7\text{H}_7\text{O}_3\text{N}_2\text{Na}$  requires  $\text{Na} = 12.12$  per cent.

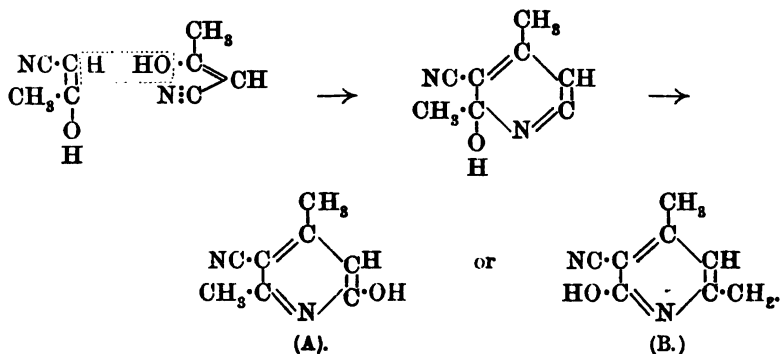
The free substance is therefore a nitro- $\psi$ -lutidostyryl.

In the preliminary note (Proc., 1901, 17, 235), I described this incorrectly as 3-nitro- $\psi$ -lutidostyryl itself. Both compounds give, on reduction, the colour-reactions characteristic of 5-amino- $\psi$ -lutidostyryl (Collie, Trans., 1898, 73, 232).

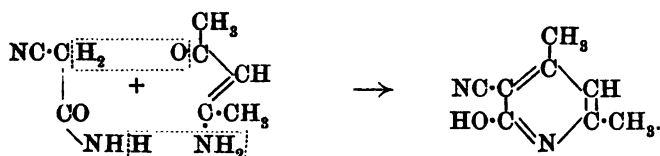
If Holtzwarth's compound be regarded as a cyano- $\psi$ -lutidostyryl, it must be represented by one or other of the two following formulæ :



and, curiously enough, its formation from 2 mols. of "isocyanacetone" can be explained on either supposition, according as it is assumed that either methyl or hydroxyl wanders in the process. The following scheme will make this clear :



The compound represented by the formula (B) is already known, and has been prepared in a manner which leaves no doubt as to its constitution, namely, by condensing acetylacetone, ammonia, and cyanacetic ester (that is, acetylacetonamine and cyanacetamide),

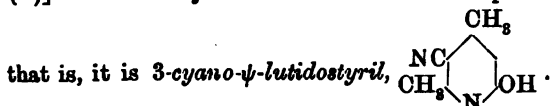


(Guareschi, *Atti R. Accad. Torino*, 1892, **28**, 330; 1898, **34**, 27; *Chem. Centr.*, 1893, ii, 648; 1899, i, 289).

As Guareschi's compound was stated to melt at 288—289°, whilst mine melted at 293° (uncorr.), I found it necessary to prepare the former substance for comparison with my product. The two compounds exhibited a remarkably close resemblance, both physically and chemically, and careful comparison was necessary to determine that the two were in reality different; indeed, it is only in their derivatives that the difference is at all decided. Guareschi's compound forms longer and more lustrous needles than mine, although possessing similar sparing solubility in the usual solvents and the same alkaloidal bitter taste. The melting point given in the literature is a *corrected* one; hence the difference between the isomerides in this respect is twelve or thirteen degrees instead of four. [I found Guareschi's compound to melt at 291° (corr.), whilst Holtzwarth's melts at 305° (corr.). A mixture of the two melts between 270° and 275°, but if this mixture be recrystallised, the product is quite different in appearance from either constituent, consisting of long, *hair-like* needles, which melt at 235—242°.] The only other physical property in which the crystals differ is their action on polarised light—Holtzwarth's compound (m. p. 305°) causing a uniform extinction at about 50° to the axis, whilst the crystals of Guareschi's isomeride (m. p. 291°) frequently produce no effect, and when an extinction is observed it is confined to half the breadth of the needles and is nearly parallel to their axis.

Chemically, too, Guareschi's compound resembles mine (1) in being non-basic; (2) in affording metallic derivatives (which are, however, less soluble than those of my compound); (3) in giving  $\psi$ -lutidostyryl, carbon dioxide, and ammonia when hydrolysed by fuming hydrobromic acid, the cyanogen group being directly displaced by hydrogen just as in the case of the isomeride (p. 103); (4) in resisting the action of sodium hydroxide, sulphuric acid, methyl iodide, &c.

This complete analogy between the two compounds leaves no doubt that both are cyano- $\psi$ -lutidostyryls, and as Holtzwarth's compound is *different* from Guareschi's—which is 5-cyano- $\psi$ -lutidostyryl [formula (B)]—it can only have the constitution represented by formula (A),



Such a compound should yield only mono-derivatives; this was actually found to be the case.

*Bromination of Holtzwarth's Compound.*—A nearly saturated solution of the substance in glacial acetic acid was mixed at  $40^{\circ}$  with a similar solution of an amount of bromine just in excess of one molecular proportion. Action soon set in, crystals separating from the solution. The liquid was diluted to separate the part remaining in solution and the product was digested first with a warm dilute solution of potassium carbonate and then with a cold very dilute solution of sodium hydroxide. The slight residue insoluble in alkalis was recrystallised from boiling glacial acetic acid, from which it separated in minute prisms, nearly insoluble in other solvents, melting at about  $270^{\circ}$  ( $280^{\circ}$  corr.), but decomposing. This substance contained 33.0 per cent. of bromine. The amount obtained was very small and insufficient to determine its nature.

On precipitating the alkaline solutions with acid, substances were obtained which ultimately proved to be identical. The major product was that extracted by sodium hydroxide; this was purified by dissolving it in the least possible quantity of a solution of sodium hydroxide and concentrating the liquid to the point of crystallisation. Long, white needles of a sodium derivative were thus obtained, easily soluble in water, and having a soapy feel. Before analysing this substance, it was recrystallised.

0.2291 gave 0.1760 AgBr. Br = 32.69.

$C_8H_6ON_2BrNa$  requires Br = 32.08 per cent.

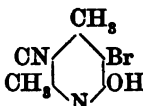
To separate the parent substance, the solution was precipitated with acid; the precipitate was well washed with boiling water, dried, and analysed, as it could not be recrystallised. It consisted of minute, white needles, which melted at  $313^{\circ}$  ( $327^{\circ}$  corr.), but underwent decomposition.

0.1929 gave 0.160 AgBr. Br = 35.3.

$C_8H_7ON_2Br$  requires Br = 35.21 per cent.

The amount of bromine found in the portion extracted by alkali carbonate was 35.79 per cent.

There can be no doubt that the substance produced was the

$\alpha$ -bromo-compound,  isomeric with the *p*-bromo-compound

(m. p.  $261^{\circ}$ ) obtained by Guareschi.

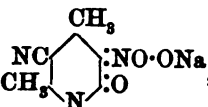
*Nitration of Holtzwarth's Compound.*—This may be effected either with fuming nitric acid and with a mixture of this acid with strong sul-

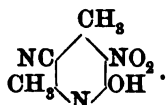
phuric acid. No change occurs below  $50^{\circ}$ , and at a higher temperature the action tends to be violent. To complete the nitration, the solution was warmed on the water-bath during a few minutes, cooled, diluted with ice, and then supersaturated with sodium hydroxide. On standing, a sparingly soluble sodium derivative of the nitro-compound crystallised out in orange rosettes. On recrystallisation, these formed long, yellow, lustrous needles, sparingly soluble in water, and quite distinct, therefore, from the salt of Collie's 5-nitro- $\psi$ -lutidostyryl-carboxylic acid (Trans., 1898, 73, 234).

0.2591 gave 0.0865  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 10.80$ .

$\text{C}_8\text{H}_6\text{O}_3\text{N}_3\text{Na}$  requires  $\text{Na} = 10.71$  per cent.

The colour is doubtless due to isomerisation to the quinonoid nitroate

, of which the white, nearly insoluble, free

substance is the  $\psi$ -acid, that is, .

On acidifying the solution of the salt, the nitro-compound was precipitated as a nearly white mass of needles, which melted at about  $240^{\circ}$ , but decomposed. After several recrystallisations from boiling water, it was obtained in long, opaque prisms which melted at  $253^{\circ}$  ( $260^{\circ}$  corr.).

As the product resembled Collie's nitro-acid, I determined nitrogen in it; although the nature of the substance prevented slow combustion, the result shows that the cyanogen group is intact.

0.1985 gave 37.2 c.c. moist nitrogen at  $85^{\circ}$  and 753 mm.  $\text{N} = 22.59$ .

$\text{C}_8\text{H}_7\text{O}_3\text{N}_3$  requires  $\text{N} = 21.80$  per cent.

The potassium salt of this substance closely resembles the sodium salt, whereas the ammonium salt is deeper in shade, forming reddish-brown prisms melting at  $251^{\circ}$  (corr.).

A further quantity of the nitro-compound was obtained by evaporating the alkaline liquid, then acidifying, and extracting with alcohol. No other product could be isolated.

An attempt to remove the cyanogen group with fuming hydrobromic acid led only to the destruction of the substance.

*Nitration of Guareschi's Compound*,  $\text{C}_8\text{H}_8\text{ON}_3$ .—This was carried out as in the preceding experiment. The nitro-compound separates on diluting the acid in pale green, lance-shaped crystals. These melt at  $261$ — $263^{\circ}$  and dissolve in a solution of potassium carbonate, forming

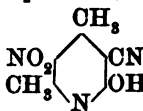
an intensely yellow liquid, which, however, on evaporation, gives a *white* solid. To remove traces of a coloured impurity, the solid was washed with a little water; the white potassium salt was then redissolved and the nitro-compound precipitated from the *orange-yellow* solution by acid. After recrystallisation, it formed spear-like, oblique plates melting at 263—264° (272° corr.). The sodium and ammonium salts were also *white* in the solid state, but gave yellow solutions.

The colour phenomena manifested by the two isomeric nitro-derivatives are obviously analogous to those given by *o*- and *p*-nitrophenol respectively, to which they correspond in the relative arrangement of the nitro- and hydroxy-groups.

On hydrolysing the nitro-compound by warming it with fuming sulphuric acid at 100°, diluting, and boiling with a nitrite (Bouveault's process), a new compound was obtained giving salts which were *orange* in the solid state. The free substance melts at 282° (corr.). Its ammonium salt dissociates on drying.

The best direct evidence of the position of the cyanogen group in Holtzwardt's compound is afforded by the behaviour of the amino-compound formed on reducing its nitro-derivative. A solution of this substance gave very characteristic colour reactions, namely, (a) a cherry-red colour on aerial oxidation in presence of ammonia; (b) with ferric chloride, a green colour, darkening to an intense indigo shade (very sensitive). Precisely similar changes were observed by Collie to take place in the case of his 5-amino- $\psi$ -lutidostyryl and its carboxy-acid (Trans., 1898, 73, 232). There can therefore be little doubt that Holtzwardt's compound is, as previously argued, the nitrile of Collie's acid.

To complete the series of reduction products, the nitro-derivative of

Guareschi's compound—presumably —was boiled with zinc

and acid as before. The solution gave merely a dull brown shade with ferric chloride, and on adding ammonia an intense blue fluorescence was developed, but no colour appeared in the liquid.

Much time was unsuccessfully devoted to attempts to establish a *direct* connection between Holtzwardt's compound and Collie's  $\psi$ -lutidostyryl-3-carboxylic acid. The ester of this acid is obtained by condensing ethyl  $\beta$ -aminocrotonate under special conditions, an interaction in every way analogous to mine (Trans., 1897, 71, 299); I am greatly indebted to Dr. Collie for a specimen of this ester with which he provided me when, at first, I had some difficulty in preparing it.

Attempts were made both to hydrolyse Holtzwardt's compound to Collie's acid, and also to transform the latter into the former. Although

neither series gave positive results, the experiments are of interest as exemplifying the stability of this class of compound. In the first instance, a solution of the substance, in 80 per cent. alcohol, was boiled during fifteen hours with potassium hydroxide in large excess. The alcohol was then boiled off and a solution of ammonium carbonate added; a copious crystallisation of the unchanged substance took place. It was to be expected that if any carboxylic salt were formed it would remain in solution; but on acidifying the filtrate only a faint turbidity was produced, and, as the expected acid (Trans., 1897, 71, 304) is practically insoluble in water, it may safely be asserted that no hydrolysis whatever had occurred. This peculiar procedure was necessitated by the fact that both the expected acid and its nitrile have the same melting point and general properties.

In addition to the methods already mentioned, heating with soda under pressure and also fusion with potash were tried; both processes, however, destroy Holtzwardt's compound completely, although it is attacked only at a high temperature. Again, the action of warm fuming sulphuric acid (which hydrolyses Guareschi's isomeride) was tried in vain, the substance being either unattacked, or sulphonated to a minute extent.


The inverse experiments are of greater interest, as throwing light on the probable cause of the resistance to hydrolysis of the nitrile group in Holtzwardt's compound; for the same inertness is shown, in a lower degree, by the carbethoxyl group in Collie's ester (m. p. 137°), and this is doubtless the cause of the failure of my efforts to synthesise the corresponding nitrile. In the first experiment, the ester was heated with excess of strong ammonia during five hours at 155—160°; practically no action occurred, the only new product being a very small quantity of the ammonium salt of Collie's acid. This is very soluble in water. No trace of an amide was observed. Similarly, the ester was quite unaffected when heated with excess of zinc-chloride-ammonia. This agent also did not act on the corresponding ethyl 6-chlorolutidinecarboxylate obtained by Collie by the action of phosphorus pentachloride on his ester (Trans., 1898, 73, 589).

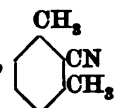
In the remaining experiments, I started with the acid (melting at 300° corr.). In preparing it, time can be saved by *fusing* the ester with potash; quite a high temperature is necessary, but the yield of acid is good, as it completely precipitated on acidifying the solution of the product. The dry ammonium salt of the acid was first heated with excess of phosphoric oxide at 300°, but on extraction with water, no trace of Holtzwardt's compound was left. On heating the ammonium salt alone, it decomposed smoothly at its melting point (about 270°) into *ψ*-lutidostyryl, carbon dioxide, and ammonia. In a final experiment, the acid was heated with 2 mols. of phosphorus pentachloride, and after



removing the oxychloride the residue was heated with excess of solid ammonium carbonate. On working up the product, a small quantity of sparingly soluble needles was separated; these, however, contained chlorine and were not investigated.

These experiments exemplify the "protective influence" of the two *o*-methyl groups on every group which becomes imprisoned between them in the ring. Several cases in which this kind of protection is

observed in benzene compounds, for example, , have been

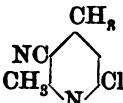
investigated by Sudborough and others. The cyanoxylene, ,

(Noyes, *Amer. Chem. J.*, 1898, 20, 792), is a particularly close analogue of Holtzwarth's compound.

There remain to be mentioned two points in which my experience has differed from Holtzwarth's; the first has reference to the by-products formed in preparing the substance  $C_8H_8ON_2$  from diacetonitrile, and the second to the action of phosphorus pentachloride on this compound. By treating the distillate obtained in preparing his compound with phenylhydrazine acetate, Holtzwarth claims to have obtained cyanacetonephenylhydrazone. I was unable to confirm this observation, but as the liquid in the flask gives the hydrazone copiously, it is possible that in Holtzwarth's case some of this liquid may have come over mechanically with the ammonia. In any case, the literature on cyanacetone is in a state of confusion, there being no less than four claimants for the name. Of these, (1) that described by Glutz (*J. pr. Chem.*, 1870, [ii], 1, 141) seems to be crude  $\psi$ -lutidostyryl; (2) Bender's sparingly soluble, beautifully crystalline compound, may be Holtzwarth's  $C_8H_8ON_2$  (*Ber.*, 1871, 4, 518), whilst the oils and syrups obtained by Matthews and Hodgkinson (*Ber.*, 1882, 15, 2679), and by James (*Annalen*, 1885, 231, 245), seem to be polymerides of the true cyanacetone of Holtzwarth, a substance which, however, seems to have but a momentary existence.

As to the action of phosphorus pentachloride on Holtzwarth's compound, the author states (*loc. cit.*, 329) that the product is gummy, but that he isolated from it a substance melting at  $175^\circ$  and giving figures agreeing with those required for the formula  $C_8H_8N_2$  [which Beilstein enters wrongly as  $C_4H_8N_2$  (*Handbuch*, 3, 1455)].

In an experiment with a pure preparation of the substance, I found it very difficult to cause any action to take place, but finally obtained a small quantity of glistening needles melting at  $165$ – $166^\circ$ , but containing chlorine not removable by alkalis. This substance is probably

the corresponding 2-chlorolutidine derivative, , or

$C_8H_7N_2Cl$ , but the quantity obtained did not permit of an analysis being made, I tried to synthesise it by the Sandmeyer method from the corresponding amino-compound (see next part), but only obtained Holtzwardt's compound instead; such abnormalities in the behaviour of 2-aminopyridines have been frequently observed.

It is evident from Holtzwardt's description of this experiment that he must have used a crude material, and I think that his compound  $C_8H_6N_2$  owes its formation to some impurity. I found, for example, that on boiling the crude compound with acetic anhydride, a small quantity of a new compound crystallising in plates melting at  $155^\circ$  was obtainable, whereas the pure substance gave no trace of this product.

## II. *The non-existence of von Meyer's "Isomeric $C_8H_8ON_2$ ."*

By acting on diacetonitrile in ethereal solution with acetyl chloride and then adding water, Holtzwardt obtained a base of the formula  $C_8H_7N_3$ , melting at  $222^\circ$  (*J. pr. Chem.*, 1889, [ii], 39, 236). The same compound was obtained by several other workers in von Meyer's laboratory by acting on diacetonitrile with a variety of reagents, such as ethyl chlorocarbonate, ethylene dibromide, alcoholic hydrogen chloride, &c., all of which act merely by removing ammonia from two mols. of diacetonitrile and inducing condensation; thus,  $2C_4H_5N_2 = C_8H_8N_3 + NH_3$ .

I have found that the best yield of this compound is obtained by simply heating diacetonitrile with zinc-chloride-ammonia until the mass solidifies; on dissolving in acid and supersaturating with soda, the new compound is precipitated and may be filtered off.

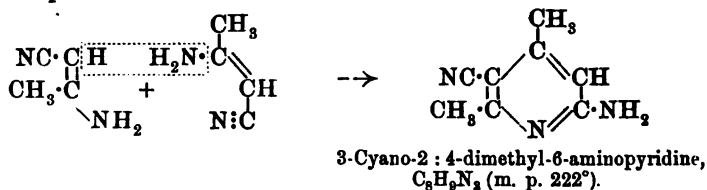
By acting on this substance with nitrous acid, von Meyer obtained a product of the formula  $C_8H_8ON_2$ , which may evidently be regarded as the corresponding hydroxy-compound; thus,  $C_8H_7N_2 \cdot NH_2 + HNO_2 = C_8H_7N_2 \cdot OH + N_2 + H_2O$  (*J. pr. Chem.*, 1895, [ii], 52, 89). This compound is described by von Meyer as melting at about  $260^\circ$ , and he pronounced it to be different from the compound of the same formula made by Holtzwardt in his laboratory in 1889, the evidence for this statement being the apparent difference in their melting points and certain differences in solubility.

I have repeated this work, and find that the two compounds are in reality identical. The solution of the compound  $C_8H_7N_3$  in dilute sulphuric acid was treated with a slight excess of nitrite and digested for some time at  $30-40^\circ$ , as it diazotises with some difficulty. On

boiling the solution, nitrogen was evolved; the compound  $C_8H_8ON_2$ , being non-basic, crystallised out on cooling, and after one crystallisation from water, melted at  $278-282^\circ$ ; on recrystallising, the melting point was raised to  $291-292^\circ$ , and under the microscope the crystals were indistinguishable from those of Holtzwarth's compound. The melting point was not depressed by mixing the two.

To confirm this result, the product was nitrated by the method described on page 107, and gave the golden needles of the sodium 'salt' of 5-nitro-3-cyano- $\psi$ -lutidostyryl there described. On reduction with zinc dust and sulphuric acid, the two colour reactions with ammonia and with ferric chloride were obtained. In all these particulars, von Meyer's product agrees with Holtzwarth's compound and no doubt can remain as to their identity. It is curious that von Meyer, having both substances at his disposal, should have been led to consider them different; yet it is evident, judging from their melting points, that his specimens must have been very impure, and hence misleading data as to solubility, &c., were given by them.

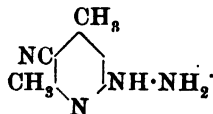
Von Meyer's "isomeric  $C_8H_8ON_2$ " (Beilstein, *Handbuch*, 4, 1151) is thus 3-cyano- $\psi$ -lutidostyryl, and as it is obtained by the diazo-reaction from the compound  $C_8H_9N_3$ , the latter must be 3-cyano-6-amino-2:4-lutidine and its formation by the direct condensation of diacetonitrile may be expressed as follows:



From these data, probable constitutions can be assigned to the obscure compounds obtained by von Meyer's students from diacetonitrile with various agents. Thus, the compound  $C_9H_{10}ON_4$  (m. p.  $145^\circ$ ), from cyanamide, which on boiling loses carbon dioxide and

ammonia, leaving Holtzwarth's  $C_8H_8ON_2$ , must be

and one of the compounds  $C_8H_{10}N_4$ , from hydrazine, must be

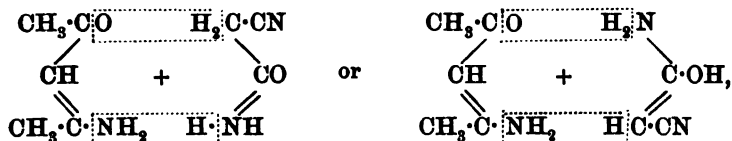


III. *ψ-Lutidostyryl-5-carboxylic Acid and some of its Derivatives.*

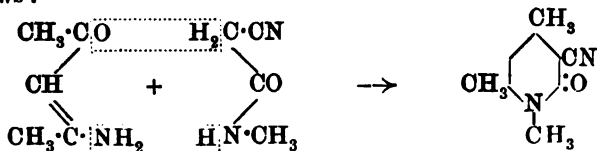
As already mentioned, every attempt to hydrolyse Holtzwardt's  $C_8H_5ON_2$  (3-cyano-*ψ*-lutidostyryl) to the corresponding acid has failed. On the other hand, I have succeeded in obtaining from Guareschi's isomeride (5-cyano-*ψ*-lutidostyryl) the corresponding amide and acid.

I may, however, first describe a number of experiments instituted to ascertain the mechanism of Guareschi's interaction, which is characterised by the ease with which it takes place without a condensing agent. The interacting substances are ethyl cyanacetate<sup>1</sup> and  $\beta$ -diketones, in the presence of a primary amine, and the reaction has been realised by its discoverer in a large number of cases (*Atti R. Accad. Torino*, 1893, 28, 330, 836; 1898, 34, 24; see also 1900, 36, 645). Of these, the simplest is that leading to the compound  $C_8H_5ON_2$  (m. p.  $289^\circ$  corr.) from acetylacetone, ethyl cyanacetate, and ammonia; but since the first two substances are both acted on by ammonia, forming respectively acetylacetonamine,  $CH_3 \cdot C(NH_2) : CH \cdot CO \cdot CH_3$ , and cyanacetamide,  $NC \cdot CH_2 \cdot CO \cdot NH_2$ , these must be considered the true interacting compounds. I found, in fact, that when the ammonia acts beforehand on only one of the substances, the condensation does not occur; that is, mixtures respectively of acetylacetone with cyanacetamide, or of acetylacetonamine with ethyl cyanacetate, do not condense; whereas, if acetylacetonamine and cyanacetamide are previously prepared free from ammonia, then the condensation occurs on mixing their aqueous solutions and gently warming.

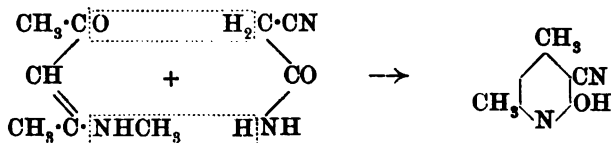
Now there are two possible explanations of this interaction,



of which only the former is a "methylene condensation." To decide between them, the experiment of heating acetylacetonamine with cyanacetmethylamide was performed. The sole product was the N-methyl-derivative of Guareschi's compound,  $C_8H_5ON_2$ , and it appears to me that its formation is not explicable by the second of the two schemes, as in this case there is no amino-group free from which water can be formed with the adjacent carboxyl group. This condensation, therefore, occurs as follows:



On the other hand, when the methyl group is introduced into the other constituent of the reaction, that is, when acetylacetone-methylamine is heated with cyanacetamide, the sole product is Guareschi's compound  $C_6H_8ON_2$ , and not its N-methyl derivative. In this case, methylamine, and not ammonia, is eliminated, and in both cases the amine originally attached to the acetylacetone is the one which [is expelled when the condensation takes place, the present reaction being expressed as follows :



Another experiment had the object of ascertaining whether the acidifying influence of the cyanogen group is the determining factor in such condensations, and this was found to be the case, for when malonamide was substituted for cyanacetamide, no condensation with acetylacetoneamine could be induced, although the only variation is the substitution for the active CN group of the  $\text{CO} \cdot \text{NH}_2$  group.

The methods of hydrolysis which proved successful with Guareschi's compound were: (1) fusion with potash; (2) treatment with warm fuming sulphuric acid. As both processes gave the same products, I shall confine myself to the latter one, which gives a good yield.

If the solution of Guareschi's compound in the acid (10 per cent.  $\text{SO}_3$ ) be diluted after standing for some time at the ordinary temperature, only unchanged substance separates; if, however, the solution has been warmed at  $100^\circ$  for a short time, nothing separates on dilution, but after several days a copious crystallisation of rosettes of needles is obtained. These are sparingly soluble in water, melt at  $209^\circ$

( $215^\circ$  corr.), and consist of the sulphate of the amide,  $\text{CH}_3 \cdot \text{C} \cdot \text{O} \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CN} \cdot \text{OH} \cdot \text{NH}_2$ ;

they are not affected by acetic anhydride, and when treated with ammonia or boiled with solution of potassium carbonate give the amide which melts at  $220$ — $221^\circ$  ( $227^\circ$  corr.), is quite easily soluble in water, and appears to be dimorphous, forming at first hard granules, which on recrystallisation give small, flat needles with square ends. Like the other substances of this class, it is easily soluble in caustic alkalis, forming a phenolic 'salt' crystallising in plates; even on boiling with potassium hydroxide, hydrolysis of the amide to the acid is slow, as is also shown by its occurrence in the potash fusion. Unlike the original product, the amide acetylates readily, and, curiously enough,

the product after recrystallisation is so like Guareschi's compound,  $C_8H_8ON_2$ , that at first I thought it had been regenerated by the dehydrating action of the reagent. It forms long, white needles melting *without darkening* at  $279-280^\circ$  ( $290^\circ$  corr.). That this substance is different from the two compounds of the formula  $C_8H_8ON_2$  was proved by the method of mixed melting points and also by an analysis which

gave results agreeing with the formula  $\text{CH}_3 \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{OH} \end{array} \text{N}$ .

0.1075 gave 13.0 c.c. moist nitrogen at  $18^\circ$  and 756 mm.  $N = 13.89$ .

$C_{10}H_{12}O_3N_2$  requires  $N = 13.49$  per cent.

It is remarkable that the amide should be so basic as to form stable salts and an acetyl derivative, and for this reason I at one time thought

that it might be an amino-acid, namely,  $\text{CH}_3 \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CO}_2\text{H} \\ \diagdown \quad \diagup \\ \text{NH}_2 \end{array} \text{N}$ , instead of

$\text{CH}_3 \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH}_2 \\ \diagdown \quad \diagup \\ \text{OH} \end{array} \text{N}$ , and to decide this point tried a number of experi-

ments, such as the isonitrile test and the action of nitrous acid followed by alkaline  $\beta$ -naphthol. The results were negative and the second formula was then definitely proved by conversion of the substance, by means of bromine and soda, into Collie's 5-amino- $\psi$ -lutidostyryl,

$\text{CH}_3 \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{NH}_2 \\ \diagdown \quad \diagup \\ \text{OH} \end{array} \text{N}$ , which gives extremely characteristic colour reactions

(see page 108, and Trans., 1898, 73, 232).

The substance (m. p.  $227^\circ$ ) is therefore really the amide of  $\psi$ -lutidostyryl-5-carboxylic acid. The next step was to obtain this acid. As the hydrolysis of the amide is effected only slowly by acids or alkalis, I tried the action of nitrous acid. On boiling the solution, nitrogen was evolved and the carboxylic acid—which is very sparingly soluble—was precipitated. This acid forms needles closely resembling its isomeride (Collie's  $\psi$ -lutidostyryl-3-carboxylic acid, m. p.  $300-304^\circ$ ), but melts at  $244^\circ$  ( $252^\circ$  corr.), and, like its isomeride, decomposes into  $\psi$ -lutidostyryl and carbon dioxide when heated above its melting point.

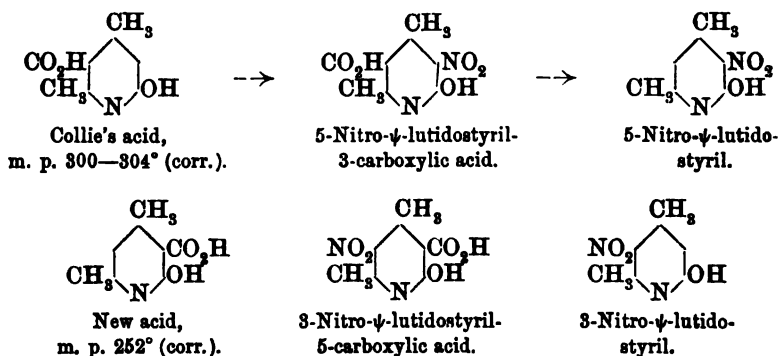
*Potassium Salt of  $\psi$ -Lutidostyryl-5-carboxylic Acid*, m. p.  $252^\circ$  (corr).—This was prepared by adding a solution of potassium carbonate to the acid, evaporating to dryness, and crystallising from boiling alcohol. It forms long, flat needles and was dried at  $120^\circ$ .

0.1564 gave 0.0668  $K_2SO_4$ .  $K = 19.18$ .

$C_8H_8O_3NK$  requires  $K = 19.06$  per cent.

**3-Nitro- $\psi$ -lutidostyryl.**—In preparing this compound, I followed Collie's description of the processes used in producing 5-nitro- $\psi$ -lutidostyryl (Trans., 1898, 73, 231). On nitrating the acid melting at  $244^\circ$ , I obtained 3-nitro- $\psi$ -lutidostyryl-5-carboxylic acid in the form of white, sparingly soluble needles melting at  $225\text{--}227^\circ$  (corr.), and giving intensely orange salts. On reduction in acid solution, the solution gave the same brown coloration with ferric chloride as its nitrile (the amino-derivative of Guareschi's compound, see p. 108) gives.

On heating the above nitro-acid at  $260^\circ$  until the evolution of carbon dioxide ceases, it is transformed into 3-nitro- $\psi$ -lutidostyryl, which on recrystallisation forms pale, shining leaflets moderately soluble in water and melting at  $260^\circ$  (corr.), and on reduction gives a reddish-brown coloration with ferric chloride. The analogy with Collie's work in this field is brought out by the following scheme :



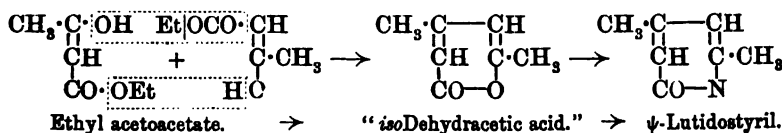
#### *The Formation of $\psi$ -Lutidostyryl from Ethyl Acetoacetate.*

Duisberg (*Annalen*, 1882, 213, 174), by heating ethyl acetoacetate with excess of ammonia, evaporating, and heating the resulting gum at  $80^\circ$ , obtained a compound decomposing at about  $280^\circ$  and eventually giving figures approximating to those required for the formula  $C_8H_8ON_2$ .

Thinking that this might be Holtzswart's compound, I tried to obtain it by heating ethyl acetoacetate with an equal bulk of strong ammonia in a sealed tube during 2 hours at  $150^\circ$ . The product was an oil containing crystals, but the latter were merely ammonium carbonate. On evaporating the thick filtrate from these, a brown gum was left which was kept on the water-bath for some time and then boiled with water and excess of animal charcoal. On concentrating the pale filtrate, I

obtained crystals which, after purification by repeated crystallisation from water, melted at 173—175° (177—179° corr.), and behaved in all respects as *ψ-lutidostyryl*.

This had evidently been formed from *isodehydracetic acid*, the first stage in the condensation of ethyl acetoacetate.



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### XIII.—*The Determination of Available Plant Food in Soils by the use of Weak Acid Solvents.*

By ALFRED DANIEL HALL, and FRANCIS JOSEPH PLYMEN.

IN the analysis of soils, it has been customary of late years to employ a weak acid solvent in order to extract those mineral constituents, phosphoric acid and potash in particular, which are present in the soil in such a state of combination as to be readily taken up by the crop. The phosphoric acid and potash thus extracted have been termed the "available," as distinct from the total, amounts of the same substances which can be extracted by hot, strong hydrochloric acid, or other solvent, which completely breaks up the soil. It is claimed that better indications of the comparative richness or poverty of the soil and of the need or otherwise for special mineral manures can be obtained by determinations of the available rather than of the total constituents, the information supplied by the latter being often not in accord with the results of cropping.

Although chemists are agreed generally about the value of weak solvents in the analysis of soils, considerable diversity of opinion exists as to the acid to use and the theoretical basis on which its action depends. Dilute acetic acid, originally suggested by H. von Liebig, was used by Dehérain (*Ann. Agron.*, 1891, 17, 445). An aqueous solution of carbon dioxide has been worked with in America, by Gerlach (*Landw. Versuchs.-Stat.*, 1896, 46, 201) and by T. Schloesing (*Compt. rend.*, 1900, 131, 149). Its adoption is obviously based upon the fact that the natural soil water, by which much of the nutrient matter of



the soil is conveyed to plants, largely owes it solvent power to carbonic acid.

Petermann, in his examinations of Belgian soils (*Recherches de Chimie et Physiologie*, 1898, 3, 50), employs an ammoniacal solution of ammonium citrate for the determination of available phosphoric acid; he regards it as "veritable reactif de groupe," distinguishing between the mineral phosphate of lime and the precipitated phosphates of lime, iron, and alumina which will rapidly come into action in the soil.

Hydrochloric acid of various strengths has been used; the American Association of Official Agricultural Chemists has recommended a solution of fifth-normal strength; trials have also been made in America with hundredth-normal hydrochloric acid.

Emmerling (*Bied. Centr.*, 1900, 29, 75) has recommended a solution of oxalic acid of 1 per cent. strength for the purpose of distinguishing between phosphoric acid combined with the alkaline earths and that combined with the sesquioxides.

Hoffmeister (*Landw. Versuchs.-Stat.*, 1898, 50, 363) suggests an ammoniacal solution of humic acid for estimating the relative values of different forms of phosphoric acid, and Maxwell (*J. Amer. Chem. Soc.*, 1899, 21, 415), in his examination of Hawaiian soils, used a 1 per cent. solution of aspartic acid, which was found to dissolve "phosphoric acid, lime, potash, and other bases out of the soil in almost the exact proportions that these elements have been found in the waters of discharge and in which they are removed by cropping."

T. Schloesing, jun. (*Compt. rend.*, 1899, 128, 1004), working with dilute nitric acid of various strengths, found that as the strength of the acid was increased, the amount of phosphoric acid dissolved first increased, then remained stationary during a certain range, and then began to increase again; at which point, and not before, iron began to appear in the solution. He concludes that this stationary proportion of phosphoric acid indicates the amount of readily available calcium phosphates and that the beginning of the attack upon the ferric phosphate marks the point at which all the available phosphoric acid has passed into solution.

But of all the dilute acids, none has been more widely applied to the determination of "available" plant food than a 1 per cent. solution of citric acid, as described by Dyer in a communication to this Society (*Trans.*, 1894, 65, 115), the 1 per cent. citric acid solution being taken as approximating both to the nature and average strength of the natural solvent, the root sap.

It is, however, doubtful if sufficient data exist upon which to base any *a priori* decision as to the best acid and strength to employ; the

state of combination of the phosphoric acid and potash in the soil, the nature of the root sap, and the part it plays in obtaining mineral matter from the soil as compared with that which enters the plant by osmosis from the natural soil water, are all too imperfectly known to provide a theoretical basis for a method of analysis. In the present state of our knowledge, these processes can only be tested by comparing the conclusions to which they lead with the results obtained by cropping the soil; indeed, the crop alone can measure the material available in the soil.

It was in the hope of obtaining some critical results with regard to the various acids suggested for determining the available constituents in the soil that the authors have obtained a number of soils which have been the subject of field experiments, and submitted them to the action of certain of the acids indicated above. As a rule, abnormal soils have been chosen, that is, soil which are markedly deficient in available phosphoric acids or potash, as indicated by the large returns which could be obtained by the application of one or other of these substances in the shape of manure.

By the kindness of Sir J. Henry Gilbert, the authors further were enabled to examine seven samples from the Broadbalk Field at Rothamsted, which had been under wheat and continually manured in the same way for forty-two years. Sir Henry Gilbert was good enough to furnish the authors with material drawn from seven sharply contrasted plots on this classic field, sufficient for duplicate determinations of both the phosphoric acid and potash dissolved by all the solvents to be described later.

Determinations were made of both phosphoric acid and potash in the Broadbalk soils and in four other cases; the nine remaining soils were only analysed for one constituent. Arising out of the work, determinations were also made of the calcium carbonate and the organic matter in each soil, and a few other determinations were made to ascertain what degree of variation might be introduced by the strength of the acid employed and the quantity of calcium carbonate present.

#### *The Soils Examined.*

The soil samples from the Broadbalk Field, Rothamsted, were taken in October, 1893; the plots had then grown wheat continuously for fifty years and the same manures had been applied to each plot year by year, with one exception, for forty-two years (*J. Roy. Agric. Soc. Eng.*, 1884, 20, 391).

The following table shows the numbers under which the plots are described in the Rothamsted Memoirs, the manures per acre per annum, and the average yield of grain and straw :

No. of plot.	Manure per acre per annum.	Grain.	Straw.
		Bushels.	Cwt.
2b	Farmyard manure, 14 tons.....	34 $\frac{5}{8}$	32 $\frac{1}{4}$
3	Unmanured continuously .....	12 $\frac{3}{4}$	10 $\frac{3}{8}$
5	Minerals only .....	14 $\frac{1}{4}$	12 $\frac{1}{4}$
6	Minerals + 200 pounds ammonium salts	24	21 $\frac{1}{2}$
7	Minerals + 400 pounds ammonium salts	32 $\frac{1}{4}$	32 $\frac{1}{4}$
9a	Minerals + 275 pounds sodium nitrate..	34 $\frac{1}{4}$	38 $\frac{1}{2}$
16	Minerals + 800 pounds ammonium salts,		
	13 years .....	—	—
	Unmanured, 19 years.....	27 $\frac{1}{8}$	28 $\frac{3}{4}$
	Minerals + 550 pounds sodium nitrate,		
	10 years .....	—	—

In the above table, "minerals" stands for 200 pounds of potassium sulphate, 100 pounds of sodium sulphate, 100 pounds of magnesium sulphate, and 3 $\frac{1}{2}$  cwt. of superphosphate (37 per cent. soluble phosphate); ammonium salts means equal parts of sulphate and chloride of ammonium containing about 43 pounds of nitrogen, which is also that contained in 275 pounds of sodium nitrate.

If the quantities given above are translated into pounds of phosphoric acid and potash supplied and removed per acre per annum, the following approximate figures are obtained. They are partially taken from a recently published paper by Dyer on the phosphoric acid and potash in wheat soils of Broadbalk Field, Rothamsted (*Phil. Trans.*, 1901, B. 194, 235—290), and are based on the manures supplied and the analyses of the grain and straw removed :

Plot.	Phosphoric acid.		Potash.	
	Supplied.	Removed.	Supplied.	Removed.
2b	78	26	235	50
3	0	9.3	0	15
5	65	14	104	23
6	64	17	108	33
7	62	22	107	51
9a	64	26	108	50
16	35	20	50	43

Of the other soils, No. 1 is a clay soil from Essex furnished by Mr. T. S. Dymond. Some of the results obtained on this field in 1899 may be quoted as showing the response of the soil to dressings of phosphates :

Manure.	Without lime. With lime.	
Sodium nitrate, 2 cwt. ....	3.3	8.2
" " 4 cwt. superphosphate	17.8	25.4

Other results with phosphatic manures, both in this year and 1900,

confirm the need for phosphates (see *The Essex Field Experiments*, 1901, I, 28).

Soil No. 2 is a Welsh soil from Cardigan, selected by Mr. T. Parry as typical of the soils in that district which respond freely to dressings of basic slag. The experimental plots in the same field showed "astonishing results" for a dressing of 10 cwt. of basic slag, but, being in pasture, no weights can be given.

Soils Nos. 3, 6, and 10, were indicated by experiments carried out under the Bath and West of England Agricultural Society, in 1891, as likely to be deficient in available phosphoric acid, and were kindly procured for us by the occupiers, Mr. J. B. Till, of Park Farm, Thornbury, Gloucestershire; Mr. E. W. Drew, of Crichel, Wimborne, and Mr. W. H. Tremaine, of Trerice Manor, Grampound, Road, Cornwall, from the fields which had been under experiment. The following extract from the report on the trials (*J. Bath and West of England Agric. Soc.*, 1891—1892, [iv], 2, 264) shows the effect of phosphatic dressings on the mangold crop:

Plot.	Character of soil.	With 4 cwt. nitrate.	4 cwt. nitrate. ,, superphosphate.
3	Gravelly loam.....	6	32.3
6	Deep loam on chalk .....	12.7	26
10	Stone rush .....	8.7	19.7

Soil No. 4 is from strong land on the Weald Clay, near Marden, Kent; the sample was taken from an arable field immediately adjoining a hop garden which has been under experiment since 1895 by the South Eastern Agricultural College. The plots have always given large returns for the application of phosphates, as will be seen from the following table, giving the mean results 1895—1899:

Plot.	Manure per acre per annum.	Mean of 5 years' crop, cwt.
1	Nitrogen, potash, 6 cwt. phosphates .....	12.5
2	" " 8 " .....	15.1
3	" " 10 " .....	15.7
4	" " 15 " .....	16.6

On the same soil, the omission of potash gave no consistent returns; on three occasions, the plot receiving nitrogen, phosphates, and potash was superior by 9 per cent., 6 per cent., and 1 per cent. respectively; on two occasions, it was inferior by 15 per cent. and 11 per cent.; hence we may fairly conclude that the soil can supply the potash requirements of an ordinary crop (see *J. South Eastern Agric. Coll.*, 1900, No. 10, 33).

No. 5 is a sandy soil, resting on the Tunbridge Wells beds, near Frant, and is also taken from a field adjoining a hop garden which has been under experiment. In this case, phosphates above a certain

point give little return, but potash salts produce a great increase in the crop. The table sets out three years' results :

Plot.	Manure per acre per annum.				Mean crop.
1	Rape dust	15 cwt.	(= 70 lbs. nitrogen) + 0	.....	15.2
2	"	"	+ basic slag 5 cwt.	.....	15.1
3	"	"	" 10 "	.....	16.1
4	"	"	" 15 "	.....	15.4
5	"	"	" 5 + potassium sulphate 5 cwt.	.....	17.7

The only consistent increase in crop each year has been on the plot receiving potash, where the effect has also been noticeable in the character of the foliage (see *J. South Eastern Agric. Coll., loc. cit.*).

Soil No. 7 was supplied by Mr. J. Alan Murray of the University College, Aberystwyth, and was taken from grass land on a light, alluvial loam at Falcondale, which has been under experiment for 8 years, and has given marked returns for dressings of phosphatic manure. Taking the mean figures for 4 years, when phosphatic manures were applied, the excess of hay produced as compared with the plots receiving no phosphate was as follows (see *Univ. Coll. Aberystwyth, Annual Report on Field Experiments, 1900*) :

For 112 lbs. superphosphate	.....	336 lbs. per acre.
" 224 "	" .....	518 "
" 336 "	" .....	552 "
" 85 " basic slag	.....	364 "
" 170 "	" .....	713 "
" 255 "	" .....	777 "

Soils 8 and 9 were from the garden at Hamel's Park, Buntingford, Essex, belonging to Mr. H. Shepherd Cross, M.P., a soil notable for causing chlorosis in many species of plants grown there, especially in laurels, fruit trees, and chrysanthemums. Applications of superphosphate had mitigated the onset of the disease, but it is by no means certain that a deficiency in available phosphoric acid is the cause.

Soils 11 and 12 were from the experimental plots of the South Eastern Agricultural College, at Wye; the soil is a light loam resting on the chalk and as a rule shows no particular need for mineral manures. Soil 11 was from a plot which had for five consecutive years grown barley without manure. Soil 12 had also grown barley, but had received a general dressing of artificial manures, including 4 cwt. of superphosphate containing 26 per cent. of soluble phosphate and  $1\frac{1}{2}$  cwt. of potassium sulphate.

The following mean figures obtained with barley, oats, and grass in 1896 and 1897 serve to show the response the crop makes to mineral manures; the various crops are reduced to a common standard

by calculating them on a basis of 100 for the plot with the complete manure.

Plot.	Manures per acre.	Relative crop.
A. No manure.....		73
B. Nitrogen + 2 cwt. superphosphate, no potash .....		93
D. Nitrogen + $\frac{3}{4}$ cwt. potassium sulphate, no phosphoric acid ...		87
E. Nitrogen + 2 cwt. superphosphate, $\frac{3}{4}$ cwt. potassium sulphate		100

Soil No. 13 was supplied to the authors by Mr. J. L. Duncan, B.Sc., from his farm at Birgidale Knock, Rothesay, N.B. It is a deep, alluvial loam, in good heart, but gave extraordinary returns for potash in some experiments with turnips carried out by Professor J. Patrick Wright in 1895.

Manure, nil.	Phosphate only.	Nitrogen and phosphate.	Nitrogen, potash, + 1 cwt. sulphate of potash.
Crop, nil.	5.9	8.9	19.8 tons.

(See *Reports on Manuring, &c., Glasgow and West of Scotland Technical College*, 1896.)

#### *The Dilute Acids Used.*

Since the 1 per cent. solution of citric acid is so widely used, especially among chemists in this country, for the determination of available phosphoric acid and potash, it was taken as the basis of comparison, and the other acids, as far as possible, were reduced to the same strength. This seemed preferable to using the other arbitrary strengths which have been suggested, such as 1 per cent. acetic acid, 1 per cent. and one-fifth normal hydrochloric acid, especially as preliminary experiments showed that the strength of the acid is a factor in the amounts of phosphoric acid and potash dissolved. Citric acid solution containing 10 grams of the pure crystallised acid per litre is approximately one-seventh normal and is equivalent to a solution of acetic acid containing 8.57 grams per litre and one of hydrochloric acid containing 5.2 grams per litre.

The ammonium citrate solution cannot be compared in strength with the other solvents; it is made up according to Petermann's formula, and used for the estimation of phosphoric acid only: 1 litre contains 87.1 grams of ammonium citrate, rendered alkaline by 9.2 c.c. of strong ammonia (sp. gr. 0.880); 500 c.c. are digested with 50 grams of the soil for 1 hour at a temperature of 35—40°, with constant shaking.

As a source of water charged with carbonic acid, recourse was had to the "sparklet" bottles of commerce; one of the larger sized bottles holds conveniently 50 grams of soil and 500 c.c. of water. Into this a sparklet charged with liquid carbon dioxide was broken in the usual

way, the contents of the bottle were allowed to stand for a week and shaken from time to time as with the other weak acids. The larger sparklets were found by trial to contain about 4.5 grams of carbon dioxide, so that the solution within the bottle would contain a little less than 9 grams per litre, and be approximately 0.4 normal. After opening the bottle, as soon as the first effervescence has subsided, the solution must be rapidly filtered and the filtering completed before all the free carbon dioxide has diffused out of the liquid.

When chalk is present in the soil, a strong solution of calcium bicarbonate is produced in the sparklet bottle, and precipitation of calcium carbonate begins when the solution is brought into contact with the atmosphere. Preliminary tests showed that solutions of acid calcium phosphate and calcium bicarbonate can exist together until the excess of carbon dioxide is expelled, when calcium phosphate is precipitated. However, the first portions of calcium carbonate precipitated during filtering, although mixed with a little fine clay, showed no appreciable amount of phosphoric acid.

The three acids, citric, acetic, and hydrochloric, of the same titre, together with carbonic acid water, were used on the soils for the estimation of both the phosphoric acid and potash.

### *Methods of Analysis.*

The soil samples were all air-dried, gently broken in a mortar with a wooden pestle, and passed through a sieve having round holes 3 mm. in diameter. The stones retained by the sieve were rejected, the fine earth that passed the sieve was used for analysis without any further preparation.

In the case of the soils from the Broadbalk Field, the samples had already been put through a wire sieve with meshes  $\frac{1}{4}$  inch apart. The 3 mm. round sieve took out a few more stones, amounting to about 24 grams from each sample of 3 pounds, or, approximately, 1.8 per cent.

Except in the case of the ammonium citrate and the carbonic acid solutions, 200 grams of the air-dried soil were put into a Winchester quart bottle with two litres of the dilute acid, the bottle was kept stoppered and shaken whenever convenient during 7 days at the ordinary temperature of the room.

At the end of this period, the solution was filtered and an aliquot part of the extract (generally 500 c.c.) was evaporated to dryness and ignited. For the determination of phosphoric acid, the residue was attacked with hydrochloric acid, evaporated to dryness, and ignited very gently to render the silica insoluble. It was then taken up with dilute nitric acid, a few grams of ammonium nitrate were added,

with 50 c.c. of a solution of ammonium molybdate, containing 60 grams of molybdic acid per litre. The volume of the nitric acid solution was always brought to 50 c.c. before adding the ammonium molybdate, in order that the work should always be carried out under uniform conditions. The mixture was well stirred and allowed to stand in a warm place, not exceeding 40°, for 24 hours. The phosphomolybdic acid, after washing with ammonium nitrate solution, was dissolved by ammonia into a tared basin, evaporated to dryness, ignited gently over an Argand burner, and weighed. The resulting material was assumed to contain 3.794 per cent. of phosphoric acid.

In potash determinations, the ignited residue from the evaporated solution was taken up with weak hydrochloric acid and the potash determined by Tatlock's method as described by Dyer (*loc. cit.*, p. 141), the potassium platinichloride being sometimes weighed as such, and sometimes converted into metallic platinum.

The so-called "total" potash and phosphoric acid were determined on portions of the same soils that were ground until they would pass through a woven sieve of 1 mm. mesh. Twenty grams of such soil were extracted with 70 c.c. of strong hydrochloric acid containing 20.2 per cent. of pure acid (that is, the acid which results on boiling the concentrated acid under ordinary atmospheric pressure) for 48 hours on a water-bath in a loosely stoppered flask.

The amount of calcium carbonate is calculated from the amount of carbon dioxide evolved on treating the soil with dilute acid by a method described in another communication (this vol., p. 81).

Some of the carbon dioxide may be derived from magnesium carbonate, but as the factor that is wanted is the amount of "base" available in the soil, it is not necessary to attempt to differentiate between calcium and magnesium carbonates.

All the figures given are calculated as percentages on the soil in an air-dry condition; the amount of water each soil loses at 100° is also given.

## I. PHOSPHORIC ACID RESULTS.

### *Soils from the Broadbalk Field.*

In the table on p. 126, the results obtained by the action of the various acids employed on the soils from the seven plots of the Broadbalk wheat field are set out.

(1). A first inspection of the figures shows that in general citric acid dissolves the most, ammonium citrate a little less, hydrochloric acid comes next in order, then acetic acid, the carbonic acid charged water dissolving least of all. This order of solvent power is preserved in each plot. Taking the means of the quantities dissolved from the six manured plots, 2b, 5, 6, 7, 9a, and 16, it will be seen that the citric



TABLE I.

Plot.	Manuring.	Citric.	HCl.	Acetic.	CO <sub>2</sub> .	Ammonium citrate.	Strong HCl.
2b	Dung .....	0.0477	0.0224	0.0166	0.0095	0.0433	0.209
3	Unmanured .....	0.0080	0.0021	0.0011	0.0005	0.0069	0.114
5	Minerals only .....	0.0510	0.0360	0.0098	0.0058	0.0388	0.228
6	Minerals + 200 lb. ammonium salts .....	0.0446	0.0264	0.0086	0.0031	0.0283	0.195
7	Minerals + 400 lb. ammonium salts .....	0.0402	0.0243	0.0067	0.0030	0.0266	0.191
9a	Minerals + 275 lb. sodium nitrate .....	0.0295	0.0070	0.0032	0.0021	0.0197	0.164
16	Minerals + 800 lb. ammonium salts...13 years	0.0208	0.0051	0.0016	0.0011	0.0141	0.157
	Unmanured .....19 years						
	Minerals + 550 lb. sodium nitrate .....10 years						

acid dissolves about ten times as much as the carbonic acid, about five times as much as the acetic acid, and twice as much as the hydrochloric acid (Table II).

In the case of the unmanured plot, the ratios are of the same order.

TABLE II.

Solvent.	P <sub>2</sub> O <sub>5</sub> dissolved from	
	Six manured plots.	Unmanured plot.
Citric acid .....	0.0390	0.0080
Ammonium citrate .....	0.0285	0.0069
Hydrochloric acid .....	0.0202	0.0021
Acetic acid .....	0.0077	0.0011
Carbonic acid .....	0.0042	0.0005

(2). The ratios in which the various acids dissolve phosphoric acid are not the same for each plot, as will be seen from a consideration of the following table (III), where the results are recalculated as percentages of the "total" phosphoric acid, that is, the amount dissolved by strong hydrochloric acid from each soil.

It is now seen that as the total phosphoric acid in the soil diminishes, so does the fraction which is soluble in any of the acids. Citric acid dissolves more than 20 percent. of the total phosphoric acid in the soil from the dunged plot and from the plots receiving minerals alone or minerals and ammonium salts; the percentage drops to 13.3 in the soil from plot 16, which had been for some time unmanured and at other times

TABLE III.

Plot.	2b.	3.	5.	6.	7.	9a.	16.
Total phosphoric acid.	0.209	0.114	0.228	0.195	0.191	0.164	0.157
Percentages of total dissolved by:—							
Citric acid .....	22.8	7.02	22.4	22.9	21.1	18.0	13.8
Ammonium citrate ...	20.7	6.05	17.0	14.5	13.9	12.0	8.98
Hydrochloric acid .....	10.7	1.84	15.1	13.5	12.7	4.28	3.25
Acetic acid .....	7.92	0.965	4.30	4.41	3.51	1.95	1.02
Carbonic acid .....	4.53	0.439	2.54	1.64	1.57	1.28	0.701

drained of minerals by the use of heavy dressings of nitrogenous manures, and still further drops to 7 per cent. in the soil from the unmanured plot. With the other acids, the same progression is observed. The crops first remove the more soluble portion of the phosphoric acid within the soil, and on those plots where the phosphoric acid has been reduced by cropping, the residue is in a comparatively insoluble form, attacked with increasing difficulty by the dilute acids employed.

(3). In order to compare the relative powers of attack possessed by the acids on the different plots, it is convenient to take as a standard for each plot the amount dissolved by the citric acid and reduce the results given by the other acids to this basis. The following table is thus obtained:

TABLE IV.

Amount dissolved by	Plot 2b.	3.	5.	6.	7.	9a.	16.
Citric acid .....	100	100	100	100	100	100	100
Ammonium citrate ...	90.8	86.2	76.1	63.5	66.2	66.8	67.8
Hydrochloric acid .....	46.9	26.2	70.6	59.2	60.4	23.7	24.5
Acetic acid .....	34.8	13.7	19.2	19.3	16.7	10.8	7.7
Carbonic acid .....	19.9	6.2	11.4	7.0	7.5	7.1	5.3

It is clear that some difference exists between the actions of the various acids; if a given acid has twice the solvent power of another in dealing with one soil, it does not follow that the same ratio will be preserved on passing to a soil of a different type.

The solution of hydrochloric acid has about two-thirds the solvent power of the citric acid in dealing with soil from the group of plots 5, 6, and 7, which receive minerals alone or with ammonium salts; one-

half with the soil from 2b, which contains much organic matter; and less than one-fourth with the soils from plots 9a and 16, where the minerals have been accompanied by nitrate.

When compared with citric acid, acetic acid also dissolves a smaller proportion of the phosphates in the soils from the nitrated plots 9a and 16, but a higher proportion than usual when dealing with the dunged plot 5.

Carbonic acid dissolves a fairly constant proportion of the phosphates dissolved by the citric acid except in dealing with the dunged plot, when its solvent powers are comparatively high.

The attack of ammonium citrate is relatively speaking at its best in dealing with the dunged plot and with the continuously unmanured plot.

(4). Turning now to the practical question, which acid yields results most in accord with the past history of the plots, it will be convenient to arrange the results in a fresh form. In the following table (V), the amount of phosphoric acid dissolved from plot 5 (minerals only) will be taken as the standard of comparison, thus showing the variation caused by the plots in the case of each acid. Plot 5 is chosen for the standard, as it has been continually manured with minerals, and but scantily cropped owing to the absence of nitrogen; it should therefore contain the greatest amount of "available" phosphoric acid.

TABLE V.

	Total.	Citric.	Ammonium citrate.	HCl.	Acetic.	CO <sub>2</sub> .
Plot 5.....	100	100	100	100	100	100
„ 2b ...	91.9	93.5	112	62.2	169	164
„ 6.....	85.5	73.0	87.4	73.3	87.8	53.5
„ 7.....	83.8	68.8	78.8	67.5	68.4	51.7
„ 9a ...	71.9	57.8	50.8	19.4	32.7	36.2
„ 16.....	68.9	40.8	36.4	14.2	16.3	19.0
„ 3.....	50.0	15.7	17.8	5.8	11.2	8.6

It is seen that all the weak solvents give more trustworthy information about the soil than the strong hydrochloric acid does. With the strong hydrochloric acid, the variation in passing from the richest plot, 5, continuously manured with superphosphate and very scantily cropped, to the poorest plot, 3, which has been cropped without manure for 50 years, is only 100 : 50, whereas with other acids the ratio varies from 00 : 17.8 to 100 : 5.8. With a few exceptions, each of the acids would set the plots in the same order of fertility; the ratios of

attack shown by citric acid and ammonium citrate are fairly similar, those of acetic and carbonic acids are still more alike.

Acetic and carbonic acids and ammonium citrate rate 2b, the dunged plot, as richer than 5, the plot which receives minerals only.

Hydrochloric acid rates the dunged plot very low, below 6 and 7, receiving mineral manures with ammonium salts; hydrochloric acid also rates 9a, the nitrated plot, very low, extracting less than one-third as much from this plot as from plots 6 and 7, whereas citric acid would make this plot almost as rich as 6 and 7.

With the variable factors introduced by the long-continued use of dung, ammonium salts, and nitrate respectively, it would be difficult to say which of these plots would be shown by cropping as relatively the richest in phosphoric acid; the surplus of the phosphoric acid supplied as manure over that removed in the crop during the last 42 years gives some figures wherewith to form an opinion, but one that does not take into account the different states of combination into which the phosphoric acid has entered in the soil.

The following table compares the surplus of phosphoric acid added to the soil during the last 50 years with the amounts removed from each plot by the various acids, assuming for the fine earth down to the depth of 9 inches, an average weight of 2,500,000 lbs. per acre. The figures are in pounds per acre.

TABLE VI.

	Surplus $P_2O_5$ retained by soil.	$P_2O_5$ dissolved by				
		Citric.	Ammonium citrate.	HCl.	Acetic.	$CO_2$ .
Plot 5.....	2582	1275	970	900	245	145
„ 2b ...	2619	1198	1082	560	415	237
„ 6.....	2355	1115	707	660	215	77.5
„ 7.....	1985	1005	665	607	167	75
„ 9a ...	1885	788	492	175	80	52.5
„ 16.....	765	520	352	127	40	27.5
„ 8.....	-467	165	172	52	27.5	12.5

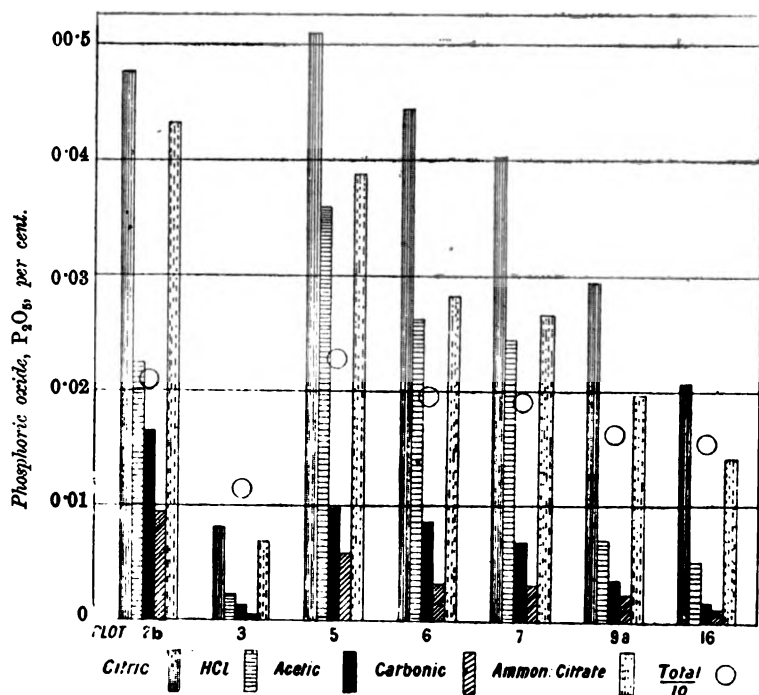
The following table shows the calcium carbonate and the loss on ignition of the soils under consideration. The loss on ignition includes both organic matter and water of hydration, but as the latter is likely to be constant in dealing with soils from the same field, the variations in the loss on ignition represent pretty nearly the variations in the amount of organic matter present.

TABLE VII.

	2b.	3.	5.	6.	7.	9a.	16.
Calcium carbonate .....	3.86	3.55	3.67	2.50	2.62	4.17	3.03
Loss on ignition .....	6.21	3.32	3.65	3.75	4.44	4.49	4.34
Hygroscopic water lost at 100° .....	2.26	1.92	1.85	2.03	1.92	2.06	2.33

The amounts of either calcium carbonate or organic matter present in the soils do not shed any consistent light on the different rates of attack shown by the solvents employed. The amount of calcium carbonate present is in no case sufficient to neutralise the acids, for which purpose about 15 grams of the carbonate would be required. Much of the calcium carbonate in the soil of plots 6 and 7 has been removed by the continual use of ammonium salts, and this may explain why the hydrochloric acid dissolves far more from these plots than from the nitrated plot 9a, which is richest in calcium carbonate.

*Phosphoric acid—Broadbalk Field.*



But the acetic acid, the solvent action of which is little affected by variation in the calcium carbonate present, also dissolves less from 9a than from plots 6 and 7. On the other hand, the dunged plot is rich in calcium carbonate and is comparatively resistant to hydrochloric acid, yet it is the plot which yields the most to acetic acid.

It is noticeable that the citric acid and ammonium citrate solutions contain considerable quantities of organic matter, silica and salts of iron and aluminium. The same mineral materials are attacked by the hydrochloric acid, but are not present to any appreciable extent in the solutions in acetic and carbonic acids. The comparative action of the various acids may be most clearly seen in the diagram on p. 130, where the heights of the vertical columns are proportionate to the amounts of phosphoric acid dissolved in each case.

For purposes of comparison, the total phosphoric acid soluble in strong hydrochloric acid is added, but plotted to the smaller scale of one-tenth.

*Phosphoric Acid Results on other Soils.*

The following table shows the percentages of phosphoric acid dissolved by each of the acids from the soils 1 to 12 previously described, arranged according to the total amount of phosphoric acid they contain :

TABLE VIII.

Soil.	Citric.	HCl.	Acetic.	Carbonic.	Ammonium citrate.	Strong HCl. Total.
1	0·0055	0·0024	0·0007	0·0033	0·0080	0·073
2	0·0085	0·0013	0·0007	0·0018	0·0295	0·089
3	0·0100	0·0035	0·0016	0·0030	0·0128	0·089
4	0·0029	0·0021	0·0007	0·0017	0·0104	0·104
5	0·0082	0·0031	0·0011	0·0023	0·0099	0·110
6	0·0033	0·0003	0·0003	0·0008	0·0122	0·112
7	0·0133	0·00435	0·0006	0·0011	0·0182	0·118
8	0·0210	0·0067	0·0016	0·0019	0·0210	0·121
9	0·0085	0·0040	0·0016	0·0022	0·0081	0·142
10	0·0071	0·0022	0·0019	0·0022	0·0089	0·145
11	0·0240	0·0167	0·0056	0·0014	0·0166	0·152
12	0·0420	0·0360	0·0120	0·0089	0·0540	0·163

(5). It is at once seen that the order in which the soils are arranged according to the total phosphoric acid is not the order of their relative richness in "available" phosphoric acid as judged by any one of the dilute solvents. This is only to be expected, considering the very different types of soil here brought together. The results generally afford

strong confirmation of the practical value of dilute solvents in judging of the need of a given soil for a phosphatic manure. With three exceptions, all the soils contain more than 0.1 per cent. of total phosphoric acid, which has been regarded as sufficient for fertility; yet the cropping tests of these soils show that only two, 11 and 12, are at all properly furnished with phosphoric acid. If, on the contrary, Dyer's limit of 0.01 per cent. of phosphoric acid soluble in 1 per cent. citric acid be taken as a criterion, the two latter soils are sharply distinguished from the rest, as containing 0.024 and 0.042 per cent. respectively, and the others with two exceptions would be rated as in need of phosphoric acid.

With acetic acid as a solvent and a limit of 0.0025 per cent. of phosphoric acid soluble, all the soils except the two, 11 and 12, known to be provided with phosphoric acid, would be rated as in need of a phosphatic manuring.

(6). The action of the different acids can be best reviewed by plotting them as before, and also by recalculating the results in terms of the amounts dissolved by citric acid from each soil, compare Table IX (p. 133) with Table IV (p. 127).

Table X. (p. 133) shows the calcium carbonate, the hygroscopic moisture, and the loss on ignition for each soil.

In Table XI (p. 133) the soils 1 to 12 are arranged as the Broadbalk soils in Table V (p. 128); that is, one soil is taken as a standard of comparison (in this table, No. 5, which is known to be very slightly if at all in need of phosphatic manuring); the phosphoric acid dissolved by each acid from this plot is called 100, and the amounts dissolved by the same acid from the other plots are reduced to this standard.

An inspection of the diagram (p. 134) shows that citric, acetic, hydrochloric and carbonic acids agree, with one or two exceptions, as to the comparative richness in available phosphoric acid of any plot. The vertical columns representing the acids rise and fall together in passing from plot to plot, as was the case with the Broadbalk soils.

The ammonium citrate, however, gives results essentially different; it rates soil 2 as better than 3, the other acids make 3 distinctly richer than 2; again, it rates 4 below 5, contrary to the relative position assigned to these two soils by the other acids and by cropping experiments.

From all the soils 1—8, 10, and 12, ammonium citrate extracts more than citric acid, a result never obtained with any of the Broadbalk soils. The high and irregular results given by ammonium citrate as compared with the other acids may probably be attributed to the comparative richness of these soils in organic matter and their poverty in calcium carbonate. The soils, 2, 4, 6, 7, and 8, which are rated

TABLE IX.—Percentages of  $P_2O_5$  dissolved by other solvents calculated on that taken up by citric acid.

Soil.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Citric acid .....	100	100	100	100	100	100	100	100	100	100	100	100
Ammonium citrate .....	144	347	128	362	121	370	137	100	94.8	126	69.2	129
Hydrochloric acid .....	42.6	15.4	35.0	73.2	37.8	9.1	32.7	31.9	47.1	31.1	39.6	85.7
Acetic acid .....	12.7	7.6	15.9	24.4	13.9	9.1	4.5	7.5	18.9	27.5	23.8	28.6
Carbonic acid .....	58.9	15.3	29.6	60.6	27.9	24.0	8.3	9.1	25.6	31.2	5.8	21.2

TABLE X.—Calcium carbonate, the hygroscopic moisture, and the loss on ignition.

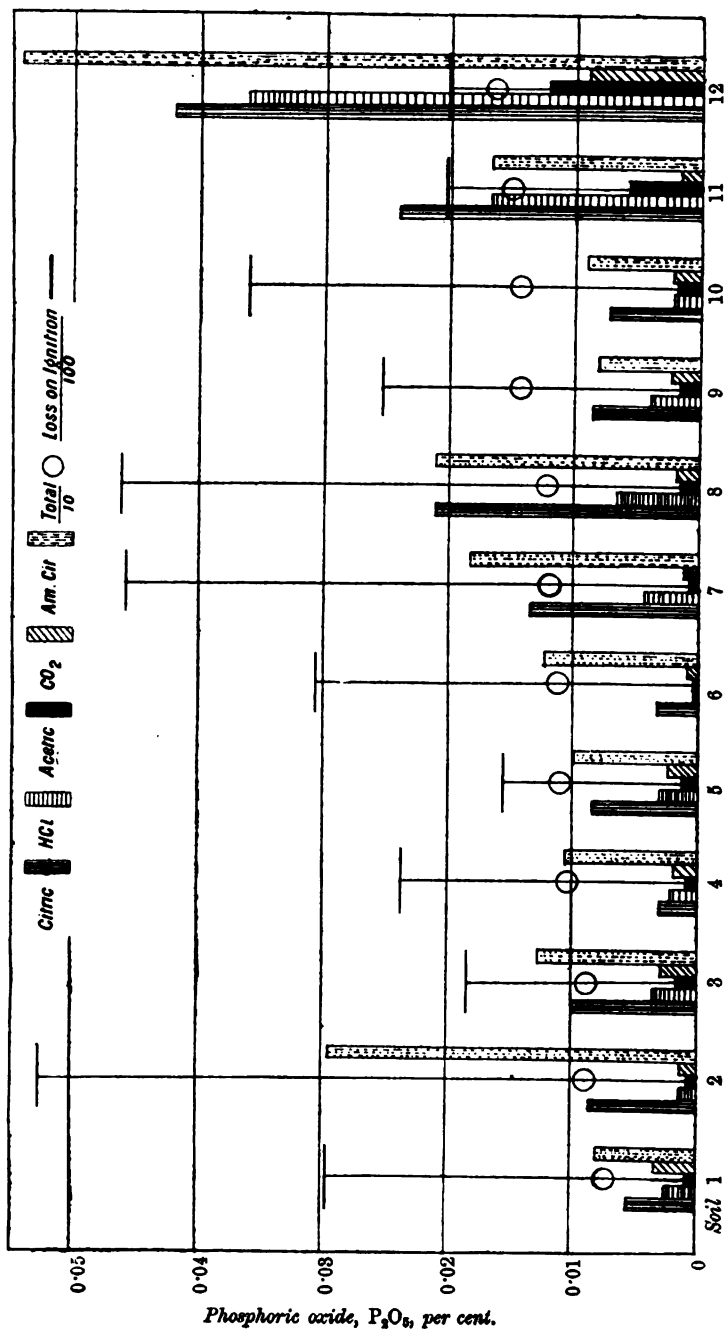
Calcium carbonate .....	0.03	trace	0.04	0.01	0.08	0.21	0.03	0.01	3.00	0.03	4.59	3.32
Loss on ignition .....	5.93	10.43	3.68	4.74	3.09	6.01	9.10	9.19	5.09	7.11	4.08	4.01
Hygroscopic water .....	4.26	6.34	2.73	3.13	2.34	4.87	2.75	4.74	3.98	2.76	2.06	1.87

TABLE XI.—Percentages of dissolved  $P_2O_5$  calculated on plot 5.

	5.	1.	2.	3.	4.	6.	7.	8.	9.	10.	11.	12.
Citric acid .....	100	67.3	104	122	85.0	40.2	162	256	104	86.0	293	512
Ammonium citrate .....	100	80.6	298	129	105	123	184	212	81.4	90.0	163	545
Hydrochloric acid .....	100	75.8	42.3	113	67.7	9.7	140	216	129	70.6	539	1161
Acetic acid .....	100	61.4	57.0	139	61.4	26.8	52.6	138	141	170	491	1053
Carbonic acid .....	100	142	56.8	129	76.0	34.9	48.0	88.0	95.2	96.1	62.0	390
Total .....	100	66.1	80.6	81.3	94.2	102	107	110	129	132	133	148



Phosphoric acid. — Other soils.



comparatively high by ammonium citrate, are rich in organic matter, 2 and 7 being the only pasture soils in the group, and 8 an artificially made soil. No. 5, which is rated low by ammonium citrate, is exceptionally deficient in organic matter.

The quantities dissolved by acetic and carbonic acids are very similar; it is to be noticed that acetic acid dissolved slightly less than carbonic acid from the soils 1—10, which are, with the exception of 9, short in calcium carbonate, but that it obtained the larger amount of phosphoric acid from soils 11 and 12 and from the Broadbalk soils which contain more than 1 per cent. of calcium carbonate.

On close inspection of the figures many differences are evident in the mode of attack of the various acids, which when followed up on a number of soils will provide information as to the forms in which the phosphoric acid of the soils is combined. The authors, however, wish in this communication to confine themselves to the question of which dilute acid yields results most in accord with the known history of the soils, and is therefore most likely to be useful in judging an unknown soil.

(7). A few figures may be here inserted showing the effect of variation in the strength of the acid used, and of additions of calcium carbonate to the soil. Dyer (*loc. cit.*) has already given figures showing that an increase in the strength of the acid results in more phosphoric acid going into solution; the authors' results are in the same sense:

TABLE XII.

Solvent.	Percentage of $P_2O_5$ dissolved.	
	Soil 7.	Soil A.
Citric acid 0·2 normal .. .. .	0·0198	0·0424
„ 1 per cent. .... .	0·0133	0·0349
„ 0·1 normal .. .. .	0·0084	0·0206

Soil A does not appear elsewhere in this paper, but was chosen as one rich in phosphoric acid and calcium carbonate, but poor in organic matter, and thus a complete contrast to soil 7.

Soil 7 was further mixed with varying amounts of calcium carbonate, obtained by grinding Iceland spar to a fine powder, and subjected to the action of citric, acetic, and carbonic acids, with the following results:

TABLE XIII.

Soil 7.	Phosphoric acid.			Potash.	
	Citric.	Acetic.	CO <sub>2</sub> .	Citric.	Acetic.
Soil only.....	0·0133	0·0006	0·0011	—	—
„ + 2 per cent. calcium carbonate	0·0090	0·0009	0·0007	0·0148	0·00714
„ + 5 „ „ „	0·0056	0·0006	0·0009	0·0092	0·00706
„ + 10 „ „ „	0·0007	0·0007	0·0009	0·0092	0·00710

These trials were not pushed further; the citric acid as it was neutralised by the calcium carbonate dissolved less and less phosphoric acid, until with 10 per cent. of calcium carbonate (more than is requisite for complete neutrality), the amount of phosphoric acid dissolved approximated to that dissolved by carbonic acid only. The solution effected by carbonic acid is independent of the calcium carbonate present, and that effected by acetic acid approximately so, because the liberated carbonic acid is an equally efficient solvent.

#### *Review of Results.*

(8). On reviewing the whole of the results, it seems very improbable that any distinction of kind can be drawn between “available” and “non-available” compounds of phosphoric acid in the soil; that is, there is not a compound or group of compounds “available,” which can be wholly removed by the plant or dissolved by an acid before the remaining compounds are attacked. Were this the case, those soils which contain only a limited amount of “available” phosphoric acid would yield all of it or none to a given solvent, and the strength of the solvent would be without influence on the result when the time limit is large.

On the contrary, the amount of phosphoric acid dissolved varies with both the nature and strength of the acid. There is no reason for regarding the phosphoric acid dissolved by the citric acid solvent as the “available” phosphoric acid in the soil rather than that which is dissolved by the acetic acid.

A soil which contains much or little “available” phosphoric acid according to one acid would be rated in the same way by another acid, even when the absolute amounts dissolved are ten times as great in one case as in another. The individual acids possess a certain selective power for different combinations of phosphoric acid and attack the different types of soils with more or less vigour, but in the main the relative action of all the acids on all the soils is alike.

The phosphoric acid of a soil must not be looked on as existing in certain compounds A, B, C, D, &c., of which A and B are insoluble and unavailable, C and D as "available"; rather A, B, C, D, &c., represent compounds possessing in each soil a coefficient of solubility, varying with the acid and with their own physical condition. The latter factor affects all the acids alike, and combined with the absolute quantity of the phosphoric acid in the soil determines the "available" phosphoric acid. The available phosphoric acid measured by a given acid depends on the coefficient of solubility possessed by the acid and the relative proportions of A, B, C, D, &c., in the soil. As soils of the same type contain A, B, C, D, &c., in roughly the same proportion, the latter factor is eliminated and the amounts of available phosphoric acid from different soils as measured by any one of the acids will be proportional to the phosphoric acid which is really "available," so that all the acids will show roughly the same relations between the soils.

Again, a soil may contain di- and tri-calcium phosphates, ferric and aluminium phosphates, and organic compounds of phosphorus like nuclein and lecithin; it would be no gain to discover a reagent which would dissolve the di- and tri-calcium phosphates only and leave the rest, for the physical conditions of these phosphates may render them less "available" to the plant than the other compounds of phosphorus present which happen to be in a favourable physical or mechanical condition for solution.

On this view the hope must be abandoned of finding any particular acid which will dissolve out the "available" phosphoric acid and leave the rest; in the results obtained by any acid, the factors are too numerous and variable to admit of exact discussion; because of its complexity, the method becomes empirical and the best acid is that which most accords with experience.

(9). In forming a conclusion as to the most suitable solvent, three things should be taken into account:

(a) The amount of phosphoric acid dissolved should show a wide variation in passing from soil to soil, so as to discriminate sharply between rich and poor soils. The largest quantity of phosphoric acid dissolved by strong hydrochloric acid from any one of the soils examined is 0.228 and the smallest 0.0727 per cent.; other things being equal, variations of this order would not discriminate so well between the soils as the variations exhibited by citric acid, which lie between 0.051 and 0.0029, or of acetic acid, which lie between 0.012 and 0.0003 per cent.

(b) The amount of phosphoric acid dissolved from normal soils should be sufficient for exact estimation, so that the variations exhibited may be of a different order of magnitude from the experimental error, which is inevitably large.

(c) The variations in the amount of phosphoric acid dissolved should so follow the known history of the soils that the reaction of an unknown soil to phosphatic manures can be predicted from its analysis. For this reason, the action of the acid should not be markedly affected by other variable constituents in the soil, such as calcium carbonate and organic matter.

*Ammonium citrate* fails to meet the last requirement; although when dealing with soils of one type, like the Broadbalk soils, its results fall into line with those given by the other solvents, yet with the other soils the indications provided by the analysis do not agree with experience. Soils 2, 7, and 8 yield comparatively large quantities of phosphoric acid to ammonium citrate solution and would be rated as sufficiently supplied with phosphoric acid, but 2 and 7 respond freely to phosphatic manures. Soils 4 and 6 yield more phosphoric acid than 5, which is quite contrary to the crop results.

These discrepancies are due to the solubility of the humus containing phosphorus compounds in the alkaline ammonium citrate solution, thus introducing material of a different order of solubility, and as the ammonium citrate solution offers no compensating advantages it may be dismissed as unsuitable.

*Hydrochloric acid* presents many anomalies of attack; it has very little solvent power for phosphoric acid when dealing with soils 1—10 which are poor in calcium carbonate; for example, it can only dissolve 0·0031 per cent. from soil 5, which is fairly provided with phosphoric acid as judged by the crop, whereas it can get 0·0021 per cent. from the unmanured plot at Rothamsted, and as much as 0·0167 per cent. from soil 11, the poorish chalky Wye soil which had been unmanured for 5 years. The Broadbalk plot 9a, which receives minerals and sodium nitrate, is rated very low; it yields only three times as much phosphoric acid as the continuously unmanured plot, and less than one-third as much as the corresponding plot 6, which receives ammonium sulphate instead of sodium nitrate. The dunged plot is also rated as inferior to the plots receiving minerals and ammonium salts.

On the whole, the results obtained with hydrochloric acid are difficult to reconcile with experience, and present no features which would justify its recommendation in place of citric acid.

*Water charged with carbonic acid* is so similar in its action to acetic acid, both in the relative and absolute amounts dissolved from the various soils, that the greater convenience of using the latter acid would cause it to be preferred.

The choice thus becomes narrowed down to *acetic* and *citric acids*.

Of these two, acetic acid better satisfies the first condition laid down above, the variations in the amounts dissolved are larger. With the

Broadbalk soils they range from 169 to 11.2, against 100 to 15.7 for citric acid (Table V). On the other soils they range from 1053 to 26.3, against 512 to 35 for citric acid (Table XI).

As regards the second criterion, the quantities of phosphoric acid dissolved by the acetic acid are very small, one-tenth to one-fifth of the amount dissolved by citric acid. The limit to be taken as indicating the need for phosphatic manuring would be about 0.002 per cent., which means the determination of only 0.001 gram of phosphoric acid in the 500 c.c. of solution commonly employed. On the other hand, the acetic acid solution is the easier to manipulate, owing to the absence of iron, alumina, silica, and dissolved organic matter; so that the experimental error is not likely to be greater than with citric acid, less indeed in unskilled hands.

As regards the interpretation of the results, it is clear that all soils deficient in calcium carbonate, as 1—8, are rated very low by acetic acid. In such soils, much of the phosphoric acid is present as precipitated ferric and aluminium phosphates, which are left practically untouched by the acetic acid, yet there is no evidence that such phosphates are quite "non-available" for the crop. Soil 5 is a case in point; acetic acid dissolves only 0.001 per cent. of phosphoric acid, yet the crops on this soil find no great need of phosphates. The Broadbalk soils are very clearly differentiated by acetic acid, the doubtful point being the comparatively low position attached to 9a and 16, the nitrate plots. The position assigned to these two plots and to 5 in the other group makes it difficult to accept acetic acid as the most "critical" solvent.

Considering the results yielded by citric acid, some difficulty of interpretation attaches to soils 2, 3, 7, and 8.

Taking the limit of 0.01 per cent. of phosphoric acid suggested by Dyer, soils 7 and 8 are above the limit with 0.0133 and 0.021 per cent. respectively; soil 3 is on the limit, and soil 2 is a little below with 0.0087 per cent.; yet the field trials indicate a need of phosphates on soils 2, 3, and 7, probably on 8 also, although as an exceptional soil it is hardly comparable with the rest.

Of all the soils examined, soils 2, 7, and 8 show the greatest loss on ignition; 2 and 7 are old pastures, 8 is a made soil containing leaf mould, and as citric acid dissolves some of the organic matter of soils, it is to this source that the high proportion of phosphoric acid yielded by these soils may be attributed. Probably the superior limit of 0.01 per cent. of phosphoric acid, as indicative of the need of phosphatic manuring, requires revision when dealing with pastures and other soils rich in organic matter.

The results yielded by soil 5 also require a little explanation; the citric acid solution only dissolves 0.0082 per cent., yet the crops show no exceptional response to phosphatic manuring. The soil is a very

light sandy loam, typical of many of the soils derived from coarse, ferruginous sandstones of secondary age. It contains very little calcium carbonate (0.08 per cent.) and little organic matter (loss on ignition 3.08 per cent.). The phosphoric acid must be largely present in this soil as ferric phosphate, and although citric acid is a better solvent than acetic acid in such cases, even the citric acid does not indicate all the phosphoric acid that seems to be "available" for crops. Gerlach (*loc. cit.*) has already indicated that typically sandy soils from which citric acid dissolves less than 0.01 per cent. of phosphoric acid may give little response to phosphatic manures.

As regards the Broadbalk soils, the results yielded by citric acid are more in accord with our knowledge of the plots than those furnished by acetic and the other acids; in particular the plots receiving nitrate 9a and 16, though below all the others except the unmanured plot, are shown as still high above the limit which may be taken to indicate the need of phosphatic manuring.

Reviewing the whole body of results, the authors consider the 1 per cent. solution of citric acid gives results which are most in accord with the known history of the soils. On soils well provided with calcium carbonate all the acids tried give very similar relative results, but this type of soil is rarely in need of phosphatic manuring, and the practical question for which the analysis is performed, whether the soil is in need of phosphatic manuring or not, usually arises in the case of soils poor in calcium carbonate.

From these soils, acetic acid can extract so little that it reduces them all to practically the same level, whilst citric acid is able to dissolve the natural phosphates of iron and alumina in a manner more in accord with the natural attack of crops.

## II. POTASH RESULTS.

Methods of analysis based upon the solvent action of weak acids must be even more empirical, when dealing with the potash in soils than with the phosphoric acid. Certain definite compounds of phosphorus, such as the organic residues, the phosphates of the sesquioxides, the neutral and acid phosphates of calcium and magnesium, exist in the soil, and are, to some extent, differentially attacked by the various solvents, but the potash compounds are far more complex and indefinite. In addition to more or less weathered silicates, like felspar and glauconite, there are indefinite compounds formed when humus and clay withdraw potash from the solution produced by the weathering of potash minerals or the application of manures.

Even the amount of potash dissolved by strong hydrochloric acid from a soil is a purely conventional figure, dependent on the strength

of the acid and the length of attack; the Broadbalk soils, for example, yield about 0.5 per cent. of potash to strong hydrochloric acid, but the total potash contained in the soil from plot 5, as determined after breaking up the soil completely with ammonium fluoride, amounted to 2.26 per cent.

The tables below show the results yielded by the soils from the same seven plots of the Broadbalk Field at Rothamsted, and by five other soils previously described; the results are also set out graphically on p. 143 in the same manner (compare p. 131) as were the phosphoric acid results.

TABLE XIV.

*Potash—soils from Broadbalk Field.*

Plot.	Manuring.	Citric.	HCl.	Acetic.	Carbonic.	Strong HCl.
2b	Dung .....	0.0400	0.0684	0.0451	0.0380	0.453
3	Unmanured.....	0.0048	0.0147	0.0082	0.0111	0.380
5	Minerals only.....	0.0458	0.0522	0.0307	0.0215	0.463
6	Minerals 200 lb. ammonium salts .....	0.0822	0.0487	0.0271	0.0151	0.530
7	Minerals 400 lb. ammonium salts .....	0.0233	0.0464	0.0240	0.0091	0.500
9a	Minerals 275 lb. sodium nitrate .....	0.0272	0.0414	0.0237	0.0238	0.440
16	Minerals 800 lb. ammonium salts.....13 years	0.0203	0.0421	0.0184	0.0145	0.504
	Unmanured .....19 years					
	Minerals 550 lb. sodium nitrate.....10 years					

On examining the results yielded by the Broadbalk soils, it is noticeable that the amounts of potash dissolved by the different acids are very similar, much more so than with phosphoric acid. Citric acid dissolves ten times as much phosphoric acid as the water charged with carbonic acid, whereas hydrochloric acid, the most energetic solvent for potash, dissolves only about three times as much as the weakest, which is again carbonic acid. On the whole, each acid leads to the same conclusions with regard to the relative richness of the plots in "available" potash, but citric acid shows the widest variation in passing from plot to plot; the ratio of 2b, the dunged plot, to 3, the unmanured plot, is 9.3 : 1 for citric acid against 4.65 : 1, 5.5 : 1, and 3.4 : 1 for hydrochloric, acetic, and carbonic acids respectively.

The results with the Broadbalk soils would indicate that the citric acid is the most "critical" solvent for "available" potash in the soil.



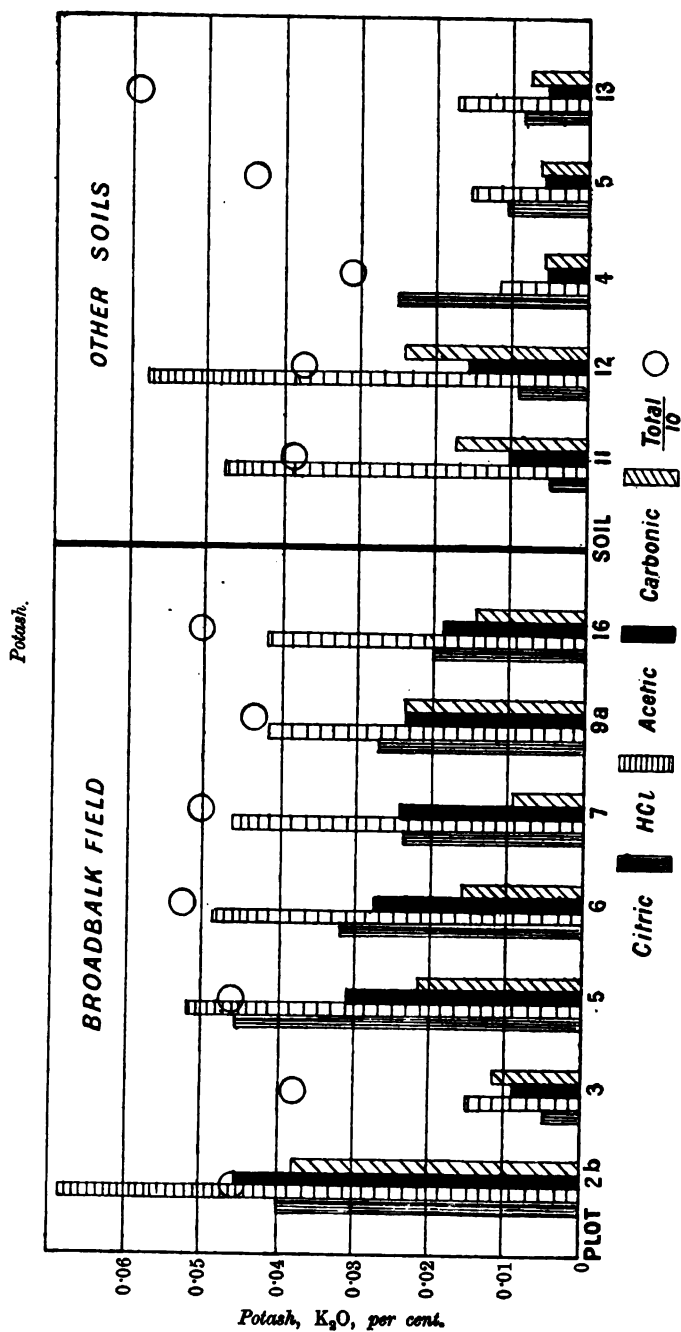


TABLE XV.

*Potash dissolved by weak acids from other soils.*

Soil.	Citric.	HCl.	Acetic.	Carbonic.	Strong HCl.	CaCO <sub>3</sub> .	Loss on ignition.	Water lost at 100°.
11	0.0050	0.0480	0.0104	0.0176	0.390	4.59	4.08	2.06
12	0.0093	0.0580	0.0156	0.0241	0.378	3.32	4.01	1.87
4	0.0250	0.0113	0.0053	0.0057	0.313	0.01	4.74	3.13
5	0.0110	0.0154	0.0059	0.0062	0.439	0.08	3.09	2.34
13	0.0085	0.0178	0.0053	0.0079	0.592	0.02	12.53	13.04

Of the other soils examined, 11 and 12 should be compared together as soils freely supplied with calcium carbonate, whereas soils 4, 5, and 13 are notably deficient in this constituent. Soils 11 and 12 are from the plots, side by side, on the same field, shown by experiment not to be particularly in need of potash manuring. No. 11 had been cropped without manure for 5 years, during which time 12 had received each year a general manure containing  $1\frac{1}{2}$  cwt. per acre of potassium sulphate. All the weak solvents show 12 as richer than 11 in "available" potash, whereas the strong hydrochloric acid would make them practically alike. The difference between them is most sharply drawn by citric acid; it is also noticeable that citric acid shows both plots as comparatively poor in "available" potash, the other three acids would rate them as comparatively rich.

Of the other three soils, field experiments have shown that 4, a strong clay, is in no need of potash manuring, but 5 and 13 gave very marked returns for potash dressings. Strong hydrochloric acid would make both 5 and 13 much richer in potash than 4; it dissolves 0.592 and 0.439 per cent. respectively from 13 and 5, against 0.313 per cent. from soil 4. Dilute hydrochloric acid would also set soil 4 below 5 and 13 in "available" potash, acetic and carbonic acids would rate them alike, the differences between the various results being of the same order as the experimental error. Citric acid alone draws a sharp distinction between the soils; it dissolves 0.025 per cent. from 4, and only 0.011 and 0.0085 per cent. respectively from the other two soils.

The results with these five soils afford most striking evidence of the practical value of weak solvents as against extraction with a strong acid in judging of the requirements of a soil for a potash manure; at the same time, they indicate it may be necessary in the light of extended experience to adopt different limits for soils of different types, for example, soils rich or poor in calcium carbonate.

Of the four weak acids employed, the authors regard citric acid as furnishing results most in accord with the history of the soils examined.

*Summary.*

The authors have compared the amounts of phosphoric acid that could be extracted from nineteen different soils by a 1 per cent. solution of citric acid, by equivalent solutions of hydrochloric acid and acetic acid, by a saturated solution of carbonic acid, and by an ammoniacal solution of ammonium citrate respectively. Seven of these soils were from plots on the Broadbalk Field, Rothamsted, which had been continuously manured in the same manner for forty-two years previously; the remaining twelve were soils of very varied origin, which had been the subject of crop experiments and whose reaction to phosphatic manuring was well marked.

In the same seven soils from the Broadbalk Field, the authors determined the potash extracted by the same dilute solvents, with the exception of ammonium citrate; five other soils of different origin, whose response or otherwise to potash manuring had been tested by experiment, were also examined in the same way.

Determinations were also made of the phosphoric acid and potash dissolved after long digestion with strong hydrochloric acid, of the loss on ignition, and of the earthy carbonates present in each soil.

The authors conclude:—(1). That no sharp line of distinction can be drawn between “available” and non-available phosphoric acid and potash in the soil, and that any process of determining the “available” constituents is an empirical one, dependent on the strength and nature of the acid used.

(2). That the weak solvents give information as to the requirements of a given soil for mineral manures of a far more trustworthy nature than that which is afforded by such a solvent as strong hydrochloric acid.

(3). That of the acids examined, the 1 per cent. solution of citric acid gives results most in agreement with the recorded history of the soil, although there is evidence that the same interpretation cannot be put on results obtained from all types of soil.

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# XIV.—Corydaline. Part VII. The Constitution of Corydaline.

By JAMES J. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER, B.Sc.

THE results obtained by oxidising corydaline with potassium permanganate and nitric acid have been described in previous communications. In the present paper, some additional experimental details are given, and the whole of the results are discussed in their bearing on the constitution of the alkaloid.

Attention has already been drawn to the resemblance which corydaline bears to berberine (Trans., 1899, 75, 670). This resemblance is not merely superficial; the two alkaloids probably differ only in some of the details of their structure. The comparison, however, must be drawn, not between corydaline and berberine, but between corydaline and tetrahydroberberine, or between dehydrocorydaline (which differs from corydaline by 4 atoms of hydrogen) and berberine. The conclusion, based on the chemical investigation, that the two alkaloids are closely related, has been confirmed by an examination of their absorption spectra, which we have found to be almost identical. The spectroscopic results will form the subject of a separate communication.

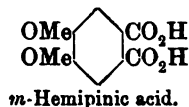
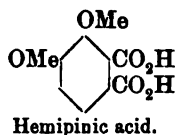
Corydaline has been analysed in recent years by various chemists, with results practically identical with those which we published in 1892 (Trans., 61, 244; Freund and Josephi, *Annalen*, 1893, 277, 1; Ziegenbein, *Arch. Pharm.*, 1896, 234, 492; Martindale, *ibid.*, 1898, 236, 214). From the analytical results, we deduced the formula  $C_{22}H_{20}O_4N$ , and Freund and Josephi the formula  $C_{23}H_{27}O_4N$ . The latter is probably the correct formula.

By the action of mild oxidising agents such as dilute nitric acid or iodine in alcoholic solution, 4 atoms of hydrogen are removed from the corydaline molecule and an intensely yellow base, dehydrocorydaline,  $C_{22}H_{16}O_4N$ , is produced, from which, by reduction, an optically inactive modification of the alkaloid may be obtained (Ziegenbein, *loc. cit.*; E. Schmidt, *Arch. Pharm.*, 1896, 234, 489; Dobbie and Marsden, Trans., 1897, 71, 657). The ease with which corydaline can be oxidised to dehydrocorydaline, and dehydrocorydaline reduced to corydaline, shows that these two substances are very closely related to one another. It will be remembered that berberine, which is a yellow base like dehydrocorydaline, and tetrahydroberberine, which resembles corydaline in being colourless, can also be readily converted the one into the other.

When corydaline is heated with a concentrated solution of hydrogen iodide, it is converted into a phenolic derivative containing four hydr-

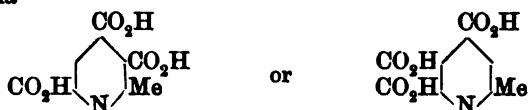
oxy groups, each molecule of corydaline yielding 4 molecules of methyl iodide. The alkaloid has therefore all its four oxygen atoms present in methoxyl groups (Trans., 1892, 61, 605).

By oxidising corydaline with potassium permanganate at the boiling point, the chief products of oxidation are hemipinic and *m*-hemipinic acids:



The presence of two benzene nuclei in the molecule is thus established (Trans., 1894, 65, 57; 1897, 71, 657; 1899, 75, 670). Along with the hemipinic acids, a small quantity of corydaldine is also obtained, the yield of which is considerably increased by conducting the oxidation at the ordinary temperature. Corydaldine has been shown to have the following constitution,  $\begin{array}{c} \text{CH}_3 \cdot \text{O} \\ \text{CH}_3 \cdot \text{O} \end{array} \text{C}_6\text{H}_2 \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , which proves the presence of an *isoquinoline* nucleus in the alkaloid (Trans., 1899, 75, 670).

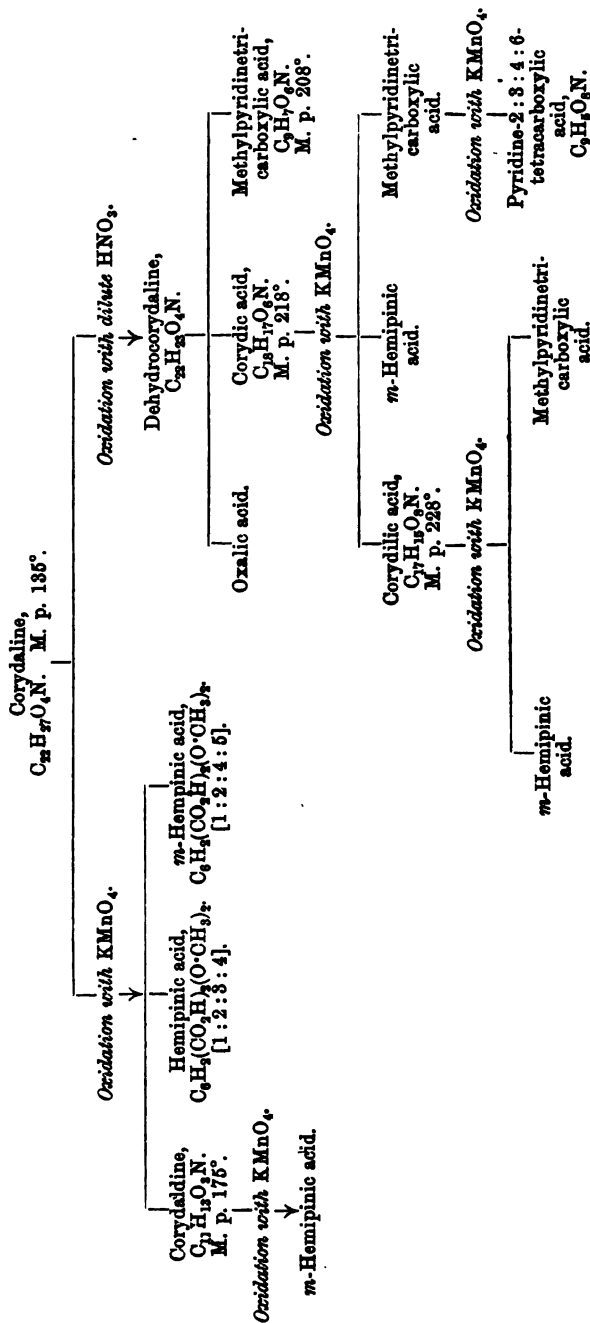
When nitric acid is used as the oxidising agent in place of permanganate, dehydrocorydaline is first produced; one of the benzene nuclei is next destroyed, and the beautiful, yellow, dibasic corydic acid,  $\text{C}_{15}\text{H}_{17}\text{O}_6\text{N} + \frac{1}{2}\text{H}_2\text{O}$ , formed. When corydic acid is in turn oxidised with permanganate at the boiling point, it is resolved into an insoluble, colourless, tribasic acid,  $\text{C}_{17}\text{H}_{15}\text{O}_8\text{N}$ , which we propose to term corydilie acid, a methylpyridinetricarboxylic acid, and *m*-hemipinic acid (Dobbie and Marsden, Trans., 1897, 71, 657). In the present paper, it is shown that the methylpyridinetricarboxylic acid has either the formula



Corydilie acid, on continued boiling with potassium permanganate, is gradually split up into a mixture of the methylpyridinetricarboxylic acid and *m*-hemipinic acid.

These results afford a basis for the discussion of the constitution of corydic acid. This acid is derived from dehydrocorydaline by the destruction of one of the benzene nuclei, and since it yields *m*-hemipinic acid as one of its oxidation products, the nucleus which is destroyed must be that from which hemipinic acid is derived. The 2-methylpyridinetricarboxylic acid, which is also one of the oxidation products of corydic acid, contains 6 atoms of carbon, exclusive of the

## Oxidation products of corydaline.



carbon atoms of the carboxyl groups. It cannot, therefore, be derived from the pyridine ring of the *isoquinoline* nucleus, since the investigation of corydaldine has shown that this pyridine ring has no side chain attached to it. The 2-methylpyridinetricarboxylic acid represents, therefore, a second ring to which the nitrogen atom, as in the case of berberine, must be common. We thus arrive at the following formula for corydic acid :

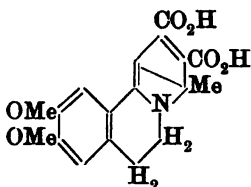


FIG. 1.—Corydic acid.

This formula accounts for the relation of the molecular formula of corydic acid to that of dehydrocorydaline; for the presence of the two carboxyl groups, and for the formation, on oxidation, of corydalic acid, the 2-methylpyridinetricarboxylic acid, and *m*-hemipinic acid. The formation of the last-named acid establishes the position of the methoxyl groups. There is no direct experimental evidence to prove that the positions of the carboxyl groups are those which we have assigned to them, rather than the positions 4 : 5, but we shall presently state our reasons for introducing a direct link between the carbon atoms 2 and 5, which limits the carboxyl groups to the positions shown in the formula.

The formula (2), which we have assigned to dehydrocorydaline follows from that of corydic acid. Perkin's formula for berberine is placed side by side for comparison (Perkin, *Trans.*, 1889, 55, 63) :

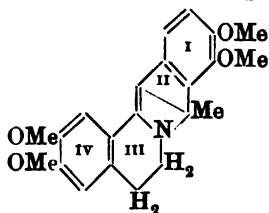


FIG. 2.—Dehydrocorydaline.

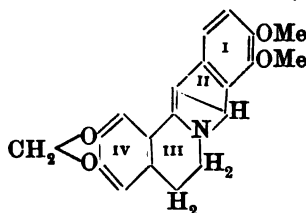


FIG. 3.—Berberine.

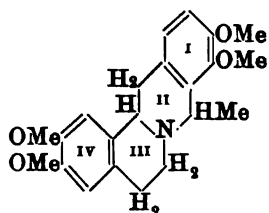


FIG. 4.—Corydaline.

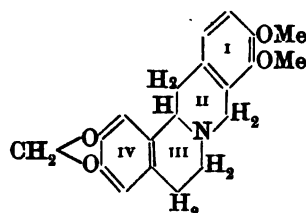


FIG. 5.—Tetrahydroberberine.

Corydaline differs from dehydrocorydaline in containing four more atoms of hydrogen. Having regard to the great ease with which corydaline can be oxidised to dehydrocorydaline and the latter substance reduced to corydaline, it may be assumed that we have to do here with a group similar to that which exists in certain anthracene and acridine derivatives, and such as Perkin has assumed to be present in berberine. The existence of a double bond between the carbon atoms 5 and 6 and of a direct bond between the carbon atoms 2 and 5 in ring II of the formula for dehydrocorydaline (Fig. 2) would explain the ease with which the one substance passes into the other.

The formula proposed for corydaline, (Fig. 4), explains the reactions and accounts for the formation of all the derivatives of the alkaloid which have been examined. By oxidation, the rings, which for convenience of reference we have numbered I and IV on the diagram, would yield hemipinic and *m*-hemipinic acids respectively, and ring II methylpyridinetricarboxylic acid. Corydaldine,  $C_{11}H_{13}O_3N$  (Fig. 6), containing rings III and IV, would result from the oxidation of corydaline in the same way as  $\omega$ -aminoethylpiperonylcarboxylic anhydride (Fig. 7) results from the oxidation of berberine :

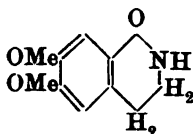


FIG. 6.—Corydaldine.

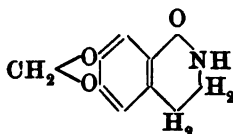
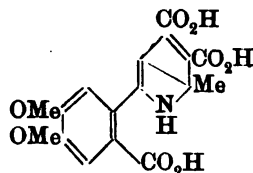
FIG. 7.— $\omega$ -Aminoethylpiperonyl carboxylic anhydride.

FIG. 8.—Corydalic acid.

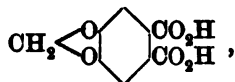
Corydic acid (Fig. 1) would be formed by the destruction of ring I, and corydalic acid (Fig. 8) from corydic acid by the oxidation of ring III.

If our formulæ are correct, they incidentally prove that Perkin's formula, which we have quoted, is to be preferred to the alternative formula suggested by him for berberine, in which the carbon atoms 2 and 5 are connected by a double bond, because, on account of the presence of the methyl group in dehydrocorydaline, no double bond is possible between the carbon atoms 2 and 5, and if a double bond existed in berberine in this position the very close resemblance between the two substances would not be satisfactorily explained.

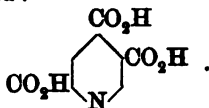
When the decomposition products of berberine are compared with those of corydaline, a close parallelism is observed between them. Both alkaloids yield hemipinic acid as a derivative of ring I. From rings III and IV,  $\omega$ -aminoethylpiperonylcarboxylic anhydride is obtained in the case of berberine, just as corydaldine is obtained from the corre-



sponding rings of corydaline. Ring IV of berberine yields hydrastic acid :



the corresponding decomposition product of corydaline being *m*-hemipinic acid. The oxidation product obtained from ring II is of special interest in the case of both alkaloids. Weidel (*Ber.*, 1879, 12, 410), by oxidising berberine with strong nitric acid, obtained as chief oxidation product berberonic acid :



We have also obtained the same acid from a new derivative of berberine, which is described in another communication. In discussing the constitution of berberine, Perkin does not take into account the occurrence of berberonic acid amongst its decomposition products. It is clear, however, that its occurrence affords important confirmation of the correctness of his formula, since it would result from ring II by the oxidation of the attached rings I and III, but could not result from ring III, which would yield cinchomeronic acid. There is thus direct evidence in the case of berberine, as well as in the case of corydaline, of the existence of a fourth closed chain in the molecule of the alkaloid. It is remarkable that both in the case of berberine and of corydaline, ring II is the more stable of the rings to which the nitrogen atom is common. From neither alkaloid has any acid corresponding to ring III been obtained. A further instance of the comparative ease with which ring III in corydaline is broken up is afforded by the formation of corydilic acid from corydic acid.

Whilst our formula for corydaline satisfactorily accounts for the similarity between this alkaloid and berberine, it also explains the absence from amongst the decomposition products of corydaline of derivatives corresponding to berberal,  $\text{C}_{20}\text{H}_{17}\text{O}_7\text{N}$ , berberilic acid,  $\text{C}_{20}\text{H}_{19}\text{O}_9\text{N}$ , oxyberberine,  $\text{C}_{20}\text{H}_{17}\text{O}_5\text{N}$ , &c., all of which have an atom of oxygen attached to the carbon atom 2 of ring II. On account of the presence of the methyl group in combination with the corresponding carbon atom in corydaline, it would be impossible for an oxygen atom to occupy this position in similar derivatives of corydaline. On the other hand, the formation of corydic acid from corydaline suggested that it might be possible to obtain a similar acid from berberine. We show in a separate communication that by the oxidation of berberine with dilute nitric acid such an acid is readily produced.

One further point remains to be dealt with, the stability of the

methyl group in ring II. With the exception of the pyridinetetracarboxylic acid (see below), all the oxidation products in which ring II is present, so far examined by us, contain this group. This is not remarkable when it is recalled that prolonged treatment with potassium permanganate in alkaline solution is required for the preparation of 2:3:4:6-pyridinetetracarboxylic acid, either from 2:4:6-trimethylquinolinecarboxylic acid (Michael, *Annalen*, 1884, 225, 121) or from flavinol (Fischer and Täuber, *Ber.*, 1884, 17, 2925). When, however, large quantities of corydaline are oxidised it might be expected that small quantities of a monocarboxylic acid should be obtained. We believe that we have had such an acid in our hands. In our earlier experiments, in which several hundred grams of corydaline were oxidised with potassium permanganate at the boiling point, a small quantity (about 1.5 grams) of a colourless nitrogenous acid which crystallised in tufts of delicate, silky needles and melted sharply at 156° (*Trans.*, 1895, 67, 17) was obtained. We were only able to make a slight examination of this substance. A nitrogen determination gave a result agreeing with that required by the formula  $C_{11}H_{24}O_4N \cdot CO_2H$  (nitrogen, found, 3.55; calculated, 3.50 per cent.). A determination of the methoxyl groups by Zeisel's method showed that the four methoxyl groups present in corydaline were also present in this acid, and the analysis of a silver salt showed that the acid possessed a high molecular weight.

We leave over for the present the full discussion of the relation between the constitution and the colour of some of the corydaline derivatives. The further investigation of the products obtained by the oxidation of corydic acid with potassium permanganate at the ordinary temperature, described below, promises to throw further light on this question. It may, however, be mentioned now that the colour seems to depend on the presence of rings II and III, since only the derivatives which contain these rings are coloured.

#### EXPERIMENTAL.

The oxidation of corydic acid with potassium permanganate (Dobbie and Marsden, *Trans.*, 1897, 71, 657) has been repeated on a larger scale, and the results already published have been confirmed; the products of oxidation are corydalic acid,  $C_{12}H_6N(O \cdot CH_2)_2(CO_2H)_3$ , a methylpyridinetricarboxylic acid,  $C_9H_7O_6N$ , and *m*-hemipinic acid.

##### *Examination of the Methylpyridinetricarboxylic Acid.*

This acid can be obtained, not only by the oxidation of corydic acid with permanganate, but also by the oxidation of corydaline with strong nitric acid in the manner followed by Weidel in the preparation of

berberonic acid from berberine (*Ber.*, 1879, 12, 410). The yield by this method is, however, unsatisfactory. The analysis and general properties of this acid have already been given (*Trans.*, 1897, 71, 657). The copper salt, obtained by adding copper acetate to a neutral solution of the acid is blue in colour, and not yellow, as previously stated. This acid is undoubtedly a methylpyridinetricarboxylic acid, as is shown by its analysis and the analysis of its salts, but it is not identical with any of the known acids of this constitution. Freund and Josephi (*Annalen*, 1893, 277, 10), from the similarity in behaviour of methylcorydaline and hydrohydrastinine, inferred that corydaline, like hydrastine, contains a methyl group attached to the nitrogen atom. By heating the acid with sodium amalgam, we failed to obtain any evidence of the formation of methylamine, and concluded from this that the methyl group was not attached to the nitrogen atom, as Freund and Josephi suggested. This conclusion was confirmed by the investigation of corydaldine which has no methyl group attached to its nitrogen atom. Further, Herzig and Meyer (*Monatsh.*, 1897, 18, 385) showed that there are only four methyl groups altogether in corydaline which can be split off by the action of hydrogen iodide, and since we have shown that there are four methoxyl groups, there can be no methyl in union with the nitrogen atom.

The methylpyridinetricarboxylic acid is an exceedingly stable substance and can be boiled for some time with a dilute solution of potassium permanganate without undergoing any appreciable amount of oxidation. When, however, it is dissolved in excess of potassium hydroxide and a solution of potassium permanganate added, it slowly undergoes oxidation, the operation requiring from eight to nine days at the temperature of the water-bath for completion. Two experiments were made, one with 3 grams and the other with 2 grams of the acid. The excess of permanganate was reduced, the alkaline solution filtered, neutralised with nitric acid and treated with calcium nitrate to remove a small quantity of oxalic acid which had been formed. After filtering from the precipitated calcium oxalate, the solution was treated with lead acetate and the precipitate filtered off and washed. On decomposing this precipitate with hydrogen sulphide, a strongly acid solution was obtained, which on evaporation yielded a residue very soluble in water and insoluble in alcohol. This residue contained inorganic matter. Its solution was found to give an insoluble salt with copper acetate which remained undissolved even when heated with acetic acid. It was therefore precipitated with copper acetate with the object of removing the inorganic matter, the blue copper precipitate filtered, well washed first with strong acetic acid and then with water, and decomposed with hydrogen sulphide. The acid obtained from the filtrate was still found, however, to be contaminated with a

small quantity of inorganic matter, from which by reprecipitation we were unable completely to purify it. We were thus unable to get an accurate determination of the melting point or a specimen of the acid in a sufficiently pure state for analysis.

So far as the qualitative examination was concerned, the acid showed all the properties and gave all the reactions of 2:3:4:6-pyridinetetracarboxylic acid obtained by Michael (*Annalen*, 1884, 225, 121) from 2:4:6-trimethylquinolinecarboxylic acid, and by Fischer and Täuber (*Ber.*, 1884, 17, 2925) from flavinol. It agreed with this acid in being very easily soluble in water and very sparingly so in alcohol; in giving with ferrous sulphate a dark cherry-red colour, and with ferric chloride a yellow precipitate. With calcium chloride, the free acid gave no precipitate, but with barium chloride a copious white precipitate. The copper salt, as already mentioned, was insoluble even in boiling acetic acid. The silver salt on ignition decomposed suddenly, swelling up and filling the crucible with reduced silver which resembled a mass of tea leaves, exactly as described both by Michael and by Fischer and Täuber.

Further information as to the identity of the oxidation product of the methylpyridinetricarboxylic acid was obtained by boiling it with strong acetic acid. When 2:3:4:5-pyridinetetracarboxylic acid is heated at 160°, 3:4:5-pyridinetricarboxylic acid is obtained, and 2:3:5:6-pyridinetetracarboxylic acid decomposes at 150° into 3:5-pyridinedicarboxylic acid. In both cases, the carboxyl groups which are eliminated are adjacent to the nitrogen atom. It was therefore to be anticipated that, under similar treatment, the tetracarboxylic acid obtained by the oxidation of the methylpyridinetricarboxylic acid would yield cinchomeronic acid by the elimination of the carboxyl groups 2 and 6, if we had rightly identified it. As a matter of fact, we found that cinchomeronic acid was produced by boiling with acetic acid, and identified without difficulty. The tetracarboxylic acid was boiled for some time with strong acetic acid and the solution evaporated to dryness. The residue was insoluble in cold and only dissolved with difficulty in hot water. The aqueous solution deposited the acid on cooling in colourless, prismatic crystals, which after purification by recrystallisation melted at 260°. The acid was insoluble in chloroform, almost insoluble in ether, and only very slightly soluble in alcohol. It gave no reaction with ferrous sulphate or with ferric chloride. Silver nitrate and lead acetate gave white precipitates when added to its aqueous solution. Calcium and barium chlorides gave no precipitate even on the addition of ammonia. The copper salt was more soluble in cold than in hot water and was precipitated by warming a cold aqueous solution; the precipitate redissolved again on cooling. The last reaction which is characteristic of cinchomeronic (pyridine-3:4-

dicarboxylic) acid, taken in conjunction with the melting point, solubility, and the reactions above described, left no doubt as to the identity of the acid which we had obtained. Cinchomeronic acid might be formed either from pyridine-2:3:4:5-tetracarboxylic acid or -2:3:4:6-tetracarboxylic acid, by the elimination of the carboxyl groups 2 and 5 or 2 and 6 respectively. It could not be derived from the 2:3:5:6-acid. The tetracarboxylic acid which we obtained not only agreed in every respect with the 2:3:4:6-acid, but differed from the 2:3:4:5-isomeride in giving no precipitate with zinc sulphate in neutral solution. The difficulty of removing inorganic matter from the tetracarboxylic acid which we obtained is characteristic of the 2:3:4:6-acid.

The methylpyridinetricarboxylic acid from corydaline must therefore have one or other of the following formulæ (Figs. 9 and 10):

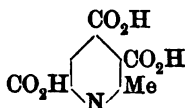


FIG. 9.

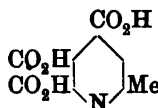


FIG. 10.

The position of one of the carboxyl groups must be adjacent to the nitrogen atom, since it follows that, when the *isoquinoline* nucleus is destroyed in the formation of methylpyridinetricarboxylic acid, the carbon atom 1, next to the nitrogen atom, must have a carboxyl group attached to it representing carbon atom 9, which is common to the benzene and pyridine rings of the *isoquinoline* nucleus (see Fig. 2).

The two remaining carboxyl groups must represent one of the rings of the corydaline molecule which has been destroyed by oxidation and must therefore occupy positions adjacent to one another.

The position of the methyl group is fixed by the following considerations. It cannot occupy the position 4, because, in that case, the only arrangement possible would be  $[\text{CH}_3 : (\text{CO}_2\text{H})_3 = 4 : 2 : 5 : 6]$ . This acid is known, and is not identical with the acid under investigation. The position 3 is likewise excluded, since, in that case, the tetracarboxylic acid obtained on oxidation would be  $[(\text{CO}_2\text{H})_4 = 2 : 3 : 4 : 5 \text{ or } 2 : 3 : 5 : 6]$ , having regard to the fact that two of the carboxyl radicles represent a ring destroyed by oxidation, and must therefore be adjacent to one another. By similar reasoning, position 5 is excluded; the methyl group must therefore occupy the position which is assigned to it in the formula. It is shown earlier in this paper that the methyltricarboxylic acid is probably  $[\text{CH}_3 : (\text{CO}_2\text{H})_3 = 2 : 3 : 4 : 6]$ , but we have no direct experimental evidence which enables us to decide between this formula and  $[\text{CH}_3 : (\text{CO}_2\text{H})_3 = 2 : 4 : 5 : 6]$ .

*Examination of Corydalic Acid,  $C_{12}H_6N(O\cdot CH_2)_2(CO_2H)_3$ .*

The analysis and description of this acid have already been published (Dobbie and Marsden, *Trans.*, 1897, 71, 657). Corydalic acid is obtained along with *m*-hemipinic and 2-methylpyridinetricarboxylic acids when corydic acid is oxidised with potassium permanganate at the boiling point. From the former it is easily separated, but it is more difficult than we at first supposed to free it entirely from the latter. Repeated recrystallisations are necessary to effect complete purification. This explains why the specimens which we analysed gave results slightly lower than the theoretical numbers. In addition to the reactions already described for this acid, we have made the following observations. Its aqueous solution gives no reaction with ferrous sulphate or ferric chloride, and no precipitate with barium chloride, calcium chloride, cadmium chloride, or copper acetate, even in presence of ammonia. From alkaline solution, corydalic acid is precipitated by the addition of excess of strong hydrochloric acid. If, however, the alkaline solution is exactly neutralised with dilute hydrochloric acid, no precipitation takes place, and a slight excess of hydrochloric acid may be added without causing the acid to separate. The solution so obtained has a faint green colour, and on standing, sometimes deposits pale, greenish-yellow crystals, which apparently consist of a hydrochloride of the acid. The crystals are very unstable, and decompose on the addition of water, leaving a residue of corydalic acid. Owing to its instability, we were unable to get this substance in a fit condition for analysis.

*Oxidation of Corydalic Acid with Potassium Permanganate.*

Corydalic acid is very stable, but on heating for several hours with potassium permanganate in alkaline solution it gradually undergoes oxidation. The acid employed was carefully purified from every trace of the methylpyridinetricarboxylic acid. About 6 grams of the pure acid were oxidised in quantities of 2 grams at a time. After removal of the manganese oxides, the alkaline solution was concentrated and precipitated with lead acetate. This precipitate, on decomposition with sulphuretted hydrogen, yielded a mixture of acids, which, on separation by fractional crystallisation, was found to consist of undecomposed corydalic acid, *m*-hemipinic acid, and the 2-methylpyridinetricarboxylic acid. The two latter acids were compared with specimens prepared directly from corydaline and found to agree in every respect.

It has already been shown that corydalic acid is tribasic, and that it contains two methoxyl groups. The following formula explains its

formation from corydic acid as well as all the facts connected with its decomposition products:

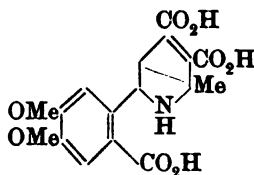


FIG. 11.

*Oxidation of Corydic Acid with Potassium Permanganate at the Ordinary Temperature.*

Corydic acid was suspended in cold water and about twice its weight of potassium permanganate added in aqueous solution in small quantities at a time. The alkaline solution was precipitated with silver nitrate and the precipitate decomposed with sulphuretted hydrogen in the usual way. The filtrate, on evaporation, deposited a bright yellow acid which, after purification by repeated recrystallisation from water, melted at 212—215°. This acid is anhydrous, and differs from corydic acid in being more soluble in cold water and in giving a precipitate with silver nitrate in neutral solution. It was dried at 100° and analysed, with the following results :

0.2503 gave 0.5506  $\text{CO}_2$  and 0.1207  $\text{H}_2\text{O}$ . C = 59.99 ; H = 5.36.

0.2086 „ 0.4621  $\text{CO}_2$  „ 0.0990  $\text{H}_2\text{O}$ . C = 60.42 ; H = 5.27.

0.2748 „ 10.6 c.c. nitrogen at 16° and 758 mm. N = 4.55.

$\text{C}_{16}\text{H}_{17}\text{O}_6\text{N}$  requires C = 60.18 ; H = 5.33 ; N = 4.39 per cent.

This acid is dibasic and forms both a normal and an acid silver salt. Its precise relation to corydic acid is still under investigation.

We have limited our investigation of corydaline derivatives and decomposition products to those substances which seemed most important for the determination of the constitution of the alkaloid, as the expense entailed has been very heavy. For the same reason, our account of some of the substances actually described is less complete than we could have wished. We hope in a future paper to supplement the information on some of the more important points which require fuller elucidation.

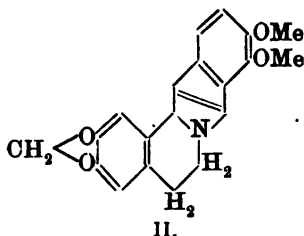
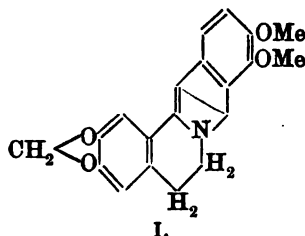
We have to express our best thanks to the Society for the liberal assistance granted to us from the Research Fund, and to Prof. W. H. Perkin, jun., for kindly giving us specimens of the decomposition products of berberine for comparison with those of corydaline.

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# XV.—*The Relationship of Corydaline to Berberine.* *Berberidic Acid.*

By JAMES J. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER, B.Sc.

PERKIN (Trans., 1890, 57, 992) has proposed the following alternative formulæ for berberine, expressing the opinion that (I) is the more probable of the two :



In the preceding paper, we have shown that the constitution of corydaline can be represented by a formula similar to I, and assuming the correctness of this formula for corydaline, that the absence of compounds corresponding to berberal,  $C_{20}H_{17}O_7N$ , berberilic acid,  $C_{20}H_{19}O_9N$ , &c., from amongst the decomposition products of corydaline is explained.\*

Whilst the absence of certain decomposition products is satisfactorily accounted for, the similarity of the formulæ assigned to the two alkaloids suggested the possibility of obtaining from berberine an acid corresponding to corydic acid, and, as a matter of fact, we found no difficulty in preparing the expected acid by a method similar to that used in the preparation of corydic acid. For convenience of reference, we shall provisionally term the substance so obtained berberidic acid.

Ten grams of berberine nitrate were suspended in two litres of dilute nitric acid (1 in 20) and heated at the temperature of the water-bath until completely dissolved. When the solution cooled, a small quantity of the new acid was deposited as a yellow, crystalline precipitate. This was filtered off, the solution neutralised with ammonia, concentrated, and precipitated with silver nitrate. The silver precipitate was decomposed with sulphuretted hydrogen and the acid separated by fractional crystallisation from a more soluble substance not yet examined, which was formed along with it. In crystallising the acid, a considerable amount of tarry matter separated out. The acid was finally freed from this and obtained in a pure state by dissolving in sodium hydroxide and precipitating with hydrochloric acid. In later preparations,

\* For further comparison of berberine with corydaline, see preceding paper.



the purification was greatly facilitated by fractional precipitation with silver nitrate, the first fraction carrying down most of the tar. The subsequent fractions were light in colour and practically pure. The yield of purified acid amounted to about 20 per cent. of the berberine nitrate used. Berberidic acid crystallises from water in radiating tufts of yellowish-brown, prismatic crystals, which have a pure yellow colour when powdered. It contains no water of crystallisation. When heated in a capillary tube, it darkens at about  $235^{\circ}$  and remains without further change, so far as can be seen, until  $285^{\circ}$ , when it melts with decomposition. It was dried at  $100^{\circ}$  and analysed, with the following results:

0.2637 gave 0.5925  $\text{CO}_2$  and 0.0866  $\text{H}_2\text{O}$ . C = 61.28; H = 3.61.

0.2831 „ 0.6344  $\text{CO}_2$  „ 0.0917  $\text{H}_2\text{O}$ . C = 61.12; H = 3.59.

0.3243 „ 13.0 c.c. nitrogen at  $16^{\circ}$  and 761.5 mm. N = 4.75.

0.2808 „ 11.0 c.c. „  $13^{\circ}$  „ 751 mm. N = 4.63.

$\text{C}_{16}\text{H}_{11}\text{O}_6\text{N}$  requires C = 61.34; H = 3.51; N = 4.47 per cent.

Berberidic acid is insoluble in cold and only sparingly soluble in boiling water. It is very sparingly soluble in boiling alcohol and insoluble in ether or chloroform. It dissolves easily in sodium hydroxide to a dark blood-red solution, from which it is precipitated by hydrochloric acid.

Berberidic acid is dibasic. All its salts, with the exception of the two silver salts, appear to be soluble. The normal silver salt is obtained by precipitating a solution of the acid, which has been neutralised with ammonia, with silver nitrate. A curdy, yellow precipitate is obtained, which darkens on exposure to light. This salt was repeatedly prepared and analysed without exact results being obtained, owing, apparently, to admixture with the acid salt.

The acid silver salt is prepared by precipitating an aqueous solution of the acid with silver nitrate. The curdy precipitate so obtained is filtered, washed, and purified by repeated recrystallisation from water. It is finally obtained in stellate clusters of beautiful, yellowish-brown needles. On heating, it decomposes suddenly with evolution of thick, brown vapours. After being dried at  $100^{\circ}$ , it was analysed with the following results:

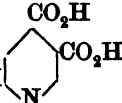
0.2470 gave 0.0828  $\text{AgCl}$ . Ag = 25.23.

0.2616 „ 0.0655  $\text{AgCl}$ . Ag = 25.04.

$\text{C}_{16}\text{H}_{10}\text{O}_6\text{NAg}$  requires Ag = 25.71 per cent.

When berberidic acid is heated with concentrated hydrogen iodide solution, no methyl iodide is evolved, a fact which proves that in the formation of this acid the ring of the berberine molecule containing the methoxyl groups is destroyed.

*Oxidation of Berberidic Acid with Potassium Permanganate.*—Five grams of berberidic acid were boiled with a dilute solution of permanganate until the permanganate was no longer reduced. The solution was filtered from the manganese oxide, concentrated, and precipitated with silver nitrate. The silver precipitate was decomposed with sulphuretted hydrogen and the filtrate from the silver sulphide evaporated to dryness. The residue was repeatedly exhausted with hot absolute alcohol, in which a considerable part of it dissolved. The portion of the residue insoluble in hot alcohol dissolved readily in boiling water, from which it separated on cooling in prismatic crystals. The acid so obtained was decolorised by boiling with charcoal and purified by repeated recrystallisation from water. It melted at  $235^{\circ}$  or  $242^{\circ}$ , according to the rate of heating. It dissolved with difficulty in cold, but was readily soluble in boiling water; it was insoluble in ether or chloroform. Its aqueous solution gave an orange-red coloration with ferrous sulphate. The acid agrees in every particular with

berberonic acid,  $\text{CO}_2\text{H}$    $\text{CO}_2\text{H}$ , which was obtained by Weidel (*Ber.*,

1879, 12, 410) by the direct oxidation of berberine with concentrated nitric acid. The melting point of berberonic acid is variously given at  $238$ — $242^{\circ}$ .

The normal silver salt, which is almost insoluble in water, was prepared by precipitating a solution of the acid, previously neutralised with ammonia, with silver nitrate. After being dried at  $100^{\circ}$ , it was analysed with the following result :

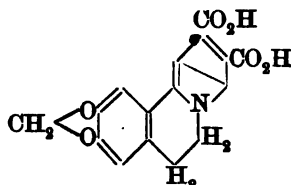
0.2978 gave 0.1798 Ag. Ag = 60.38.

$\text{C}_8\text{H}_5\text{O}_6\text{NaAg}_3$  requires Ag = 60.88 per cent.

The presence of hydrastic acid amongst the decomposition products of berberidic acid has not yet been proved. By dissolving berberidic acid in potassium carbonate and oxidising it with potassium permanganate at the ordinary temperature, a small quantity of a substance was obtained as a scum on the surface of the strongly alkaline solution. From its insolubility in potash, we suspected that this substance might be  $\omega$ -aminoethylpiperonyl carboxylic anhydride, which is insoluble in alkaline solutions. On examination, we found that it agreed in every particular with the anhydride in its neutral reaction, solubility, peculiar mode of crystallisation, and behaviour with mercuric chloride. As the amount of substance obtained was too small to admit of complete purification, the melting point observed was slightly lower than that given by Perkin.

Berberidic acid clearly bears the same relation to berberine that

corydic acid bears to dehydrocorydaline. Since it contains no methoxyl groups, it follows that the ring of the berberine molecule which yields hemipinic acid is destroyed in its formation. The occurrence of  $\alpha$ -aminoethylpiperonylcarboxylic anhydride and berberonic acid amongst its oxidation products proves that it contains the three remaining rings and that its constitution may therefore be expressed by the formula :



By oxidising berberidic acid with potassium permanganate at the ordinary temperature, a yellow derivative is obtained like that obtained from corydic acid by similar treatment.

As berberine, unlike corydaline, can be obtained at comparatively low cost, we have undertaken a more thorough investigation of berberidic acid, which we hope will throw further light on the constitution of both alkaloids, and especially on the relation between the constitution and colour of some of their derivatives.

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BANGOR.

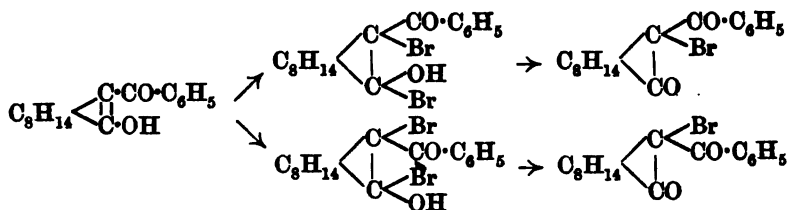
## XVI.—*Studies in the Camphane Series. Part VI.* *Stereoisomeric Halogen Derivatives of $\alpha$ -Benzoyl-* *camphor.*

By MARTIN ONSLOW FORSTER and FRANCES M. G. MICKLETHWAIT.

IN accordance with its unsaturated character, 1-hydroxy-2-benzoylcamphene, the enolic form of  $\alpha$ -benzoylcamphor, immediately decolorises a solution of bromine in an indifferent solvent. At the same time hydrogen bromide is eliminated, and if one molecular proportion of the halogen is employed, the crystalline residue obtained on evaporating the liquid has the empirical formula of benzoylbromocamphor. There is no difficulty, however, in resolving this product into two distinct substances which, although isomeric and nearly alike in chemical behaviour, are widely different in physical properties. The more soluble constituent of the mixture crystallises from alcohol in six-sided prisms, melts at  $114^{\circ}$ , has  $[\alpha]_D -10.0^{\circ}$  in benzene, and  $[\alpha]_D$

+10.3° in chloroform; the isomeride is deposited from alcohol in rectangular plates, melts at 214°, has  $[\alpha]_D -53.2^\circ$  in benzene, and  $[\alpha]_D -19.3^\circ$  in chloroform.

The method of preparation, the fact that neither substance dissolves in alkalis, and the transformation of both isomerides into 1-hydroxy-2-benzoylcamphene by the action of alcoholic potash, are circumstances which point to the conclusion that the compounds in question are  $\alpha$ -bromo-derivatives of  $\alpha$ -benzoylcamphor, and that their physical differences are the result of a difference in configuration. Theoretical considerations, moreover, led us to expect the formation of two derivatives displaying isomerism of the *cis-trans*-type, as indicated by the following formulæ (compare Lowry, *Trans.*, 1898, 73, 572):



It is evident that a similar explanation would account also for the production of two isomerides from enolic benzoylcamphor in the event of that substance being shown to have the alternative formula, namely, that of phenylhydroxymethylenecamphor,  $C_8H_{14} \begin{smallmatrix} \diagup \\ C \\ \diagdown \end{smallmatrix} \begin{smallmatrix} C(OH) \cdot C_6H_5 \\ CO \end{smallmatrix}$ , a possibility which is not yet excluded.

Several instances of this form of isomerism in the camphor series have now been established. Leaving aside the somewhat uncertain cases of the monohalogen derivatives of camphor, there remain the isomeric chlorobromocamphors, chloronitrocaphors, and bromonitrocaphors investigated by Lowry (*Trans.*, 1898, 73, 569 and 986), and the benzylbromocamphors described by Haller and Minguin (*Compt. rend.*, 1901, 133, 79). Up to a certain point, the case of the benzoylbromocamphors resembles those of the four derivatives mentioned, the difference between the two forms being, however, greater than has been observed hitherto; but an important feature distinguishes it from those already described.

In dealing with the isomeric chlorobromocamphors, Lowry records unsuccessful attempts to convert  $\alpha'$ -chloro- $\alpha$ -bromocamphor into  $\alpha$ -chloro- $\alpha'$ -bromocamphor by the action of heat and of acids (*Trans.*, 1898, 73, 581). Neither in his subsequent communication nor in the paper of Haller and Minguin (*loc. cit.*) is it stated that the chloronitrocaphor, bromonitrocaphor, or benzylbromocamphor of lower melting point can be transformed into the corresponding isomeride, and it is

probable therefore that the change cannot be effected or it would have been observed. It is in this respect that the benzoylbromocamphors differ from the foregoing disubstituted  $\alpha$ -derivatives, for the compound having the lower melting point is readily converted into the isomeride by the action of hydrogen bromide.

This transformation is the first recorded instance of stereoisomeric change on the part of a disubstituted derivative of camphor in which both substituents occupy the  $\alpha$ -position. It has therefore a direct bearing on the explanation given by Marsh in accounting for the unstable character of a specimen of bromocamphor which is described as melting at  $61^\circ$  (Trans., 1890, 57, 832; compare also Lowry, Trans., 1898, 73, 572). The validity of the explanation in question depends on the formation of an intermediate isomeride, which represents the enolic modification of the material transformed, and, in the case discussed by

Marsh, would have the formula  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CBr} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{OH} \end{array}$ . The experiments described in this paper have led us to consider this explanation improbable. In the first place, it cannot be applied to derivatives of camphor of the class to which benzoylbromocamphor belongs, and secondly, there seems to be no need for any explanation so complex, several cases of stereochemical transformation being known in which there is no room for any structural change to occur.

In general features, the benzoylchlorocamphors resemble the corresponding bromo-derivatives very closely, the two modifications which melt at  $88^\circ$  and  $219^\circ$  displaying similarity as regards solubility and crystalline form when compared respectively with the bromo-derivatives melting at  $114^\circ$  and  $214^\circ$ . It is noteworthy, however, that we have been hitherto unable to convert one isomeride into the other. Moreover, the action of sodium hypochlorite on enolic benzoylcamphor gives rise to a preponderating quantity of the benzoylchlorocamphor of the lower melting point, whilst the benzoylbromocamphor of the higher melting point is the almost exclusive product when potassium hypobromite is employed; bromine dissolved in chloroform yields a mixture of the isomerides in nearly equal parts, whilst bromine and glacial acetic acid containing sodium acetate afford chiefly the benzoylbromocamphor of lower melting point.

In describing the stereoisomeric halogen derivatives of  $\alpha$ -benzoylcamphor, we have adopted the convention suggested by Lowry (*loc. cit.*), so that the nomenclature of the new derivatives may be uniform with that of the unsymmetrical di-derivatives already prepared. Assuming that benzoylcamphor, with  $[\alpha]_D + 137.5^\circ$  in alcohol, is an  $\alpha$ -derivative, it will be noticed that the optical influence of the benzoyl radicle exceeds that of the chlorine atom, since  $\alpha$ -chlorocamphor has  $[\alpha]_D + 96^\circ$  in the same solvent; it may be concluded therefore that the di-

derivative which has a specific rotatory power least removed from that of camphor itself, is that which contains the benzoyl radicle in the  $\alpha$ -position. This modification is the one which melts at  $219^\circ$ , having  $[\alpha]_D + 26.2^\circ$  in chloroform, and is accordingly termed  $\alpha$ -benzoyl- $\alpha'$ -chlorocamphor. In the case of the bromo-derivatives, it is not so easy to decide which isomeride contains the benzoyl radicle in the  $\alpha$ -position, because the recorded values for the specific rotatory power of benzoylcamphor and of bromocamphor in alcohol are practically identical. There is reason to believe, however, that the specific rotatory power of benzoylcamphor at the moment of dissolution in alcohol is lower than  $[\alpha]_D + 137.5^\circ$ , because the substance, dissolving somewhat slowly in the cold solvent, suffers partial conversion into the enolic modification, with  $[\alpha]_D + 262^\circ$ , before it can be examined in the polarimeter; chloroform, however, which dissolves the substance very readily, yields a solution having  $[\alpha]_D + 125^\circ$ , and it is therefore probable that the optical influence of the benzoyl radicle is less powerful than that of the bromine atom, because  $\alpha$ -bromocamphor has  $[\alpha]_D + 135^\circ$ . If this is the case, the modification which melts at  $114^\circ$  and has  $[\alpha]_D + 10.3^\circ$  in chloroform must be called  $\alpha'$ -benzoyl- $\alpha$ -bromocamphor, whilst the isomeride melting at  $214^\circ$ , having a specific rotatory power more remote from that of camphor, must be regarded as having the bromine atom in the  $\alpha'$ -position;

	$[\alpha]_D$	m. p.
Camphor .....	+ $42^\circ$ ( alcohol )	—
$\alpha$ -Chlorocamphor .....	+ 96 ( „ )	—
$\alpha$ -Bromocamphor .....	+ 135 ( „ )	—
$\alpha$ -Benzoylcamphor .....	+ 125 (chloroform)	—
$\alpha'$ -Benzoyl- $\alpha$ -chlorocamphor ...	- 28 ( „ )	$88^\circ$
$\alpha$ -Benzoyl- $\alpha'$ -chlorocamphor ...	+ 26 ( „ )	$219^\circ$
$\alpha'$ -Benzoyl- $\alpha$ -bromocamphor ...	+ 10 ( „ )	$114^\circ$
$\alpha$ -Benzoyl- $\alpha'$ -bromocamphor ...	- 19 ( „ )	$214^\circ$

From this table, it will be noticed that the benzoylchlorocamphor and benzoylbromocamphor supposed to contain the halogen in the  $\alpha$ -position both melt at the lower temperature, whilst the less readily fusible modifications are assumed to have the halogen substituted in the  $\alpha'$ -position.

#### EXPERIMENTAL.



Twenty grams of 1-hydroxy-2-benzoylcamphene were dissolved in chloroform and cooled in melting ice. A cold solution of 12.4 grams of bromine in chloroform was then added in small quantities at a time,

and the pale red liquid, from which hydrogen bromide was being evolved, transferred to a basin and allowed to evaporate spontaneously. A previous experiment having shown that two compounds are produced by this means, the crystalline residue was divided into four fractions by extracting it successively with quantities of hot alcohol amounting to 100 c.c. (twice), 200 c.c., and 300 c.c., and allowing the solutions to cool.

Fraction I, weighing 6 grams, consisted of thin, transparent needles melting somewhat indefinitely at  $108-110^{\circ}$ ; a 2 per cent. solution in benzene gave  $[\alpha]_D - 15.4^{\circ}$ ; and in chloroform  $[\alpha]_D + 7.9^{\circ}$ . A large proportion being readily soluble in warm, light petroleum (b. p.  $50-90^{\circ}$ ), the whole fraction was extracted with this solvent; the solution deposited large, thin, six-sided prisms melting at  $114^{\circ}$  and giving  $[\alpha]_D - 10.0^{\circ}$  in benzene and  $[\alpha]_D + 10.3^{\circ}$  in chloroform. Recrystallisation from light petroleum did not change the specific rotatory power.

Fraction II, weighing 8 grams, consisted chiefly of needles, and melted somewhat indefinitely at  $109-111^{\circ}$ ; a 2 per cent. solution in benzene gave  $[\alpha]_D - 19.5^{\circ}$ , and in chloroform  $[\alpha]_D + 2.9^{\circ}$ .

Fraction III, weighing 2 grams, consisted of thin, rectangular plates, beginning to shrink and to change colour at about  $185^{\circ}$  and melting at  $210^{\circ}$ ; a 2 per cent. solution in benzene gave  $[\alpha]_D - 52.3^{\circ}$ , and in chloroform  $[\alpha]_D - 18.5^{\circ}$ .

Fraction IV, weighing 3 grams, consisted of thin, rectangular plates, beginning to shrink and to change colour at about  $190^{\circ}$ , and melting at  $214^{\circ}$ ; a 2 per cent. solution in benzene gave  $[\alpha]_D - 53.2^{\circ}$ , and in chloroform  $[\alpha]_D - 19.3^{\circ}$ . The properties of this fraction were not altered by recrystallisation from boiling alcohol.

*a'-Benzoyl-a-bromocamphor* is most conveniently prepared by dissolving 1-hydroxy-2-benzoylcamphene in glacial acetic acid containing  $1\frac{1}{2}$  mols. of sodium acetate and adding 1 mol. of bromine dissolved in glacial acetic acid; the white precipitate obtained on pouring this liquid into water is then collected, washed, dried, and crystallised from light petroleum. It is readily soluble in chloroform, benzene, alcohol, or light petroleum, crystallising from the last-named in large, transparent, six-sided prisms, and from alcohol in slender needles having the same crystalline form:

0.1992 gave 0.1101 AgBr. Br = 23.52.

$C_{17}H_{19}O_2Br$  requires Br = 23.88 per cent.

The substance melts at  $114^{\circ}$ , but fusion is not complete until the temperature is raised to about  $180^{\circ}$ . A solution containing 0.5 gram in 25 c.c. of benzene at  $21^{\circ}$  gave  $\alpha_D - 24'$  in a 2 dcm. tube, whence the specific rotatory power  $[\alpha]_D - 10.0^{\circ}$ ; 0.5029 dissolved in 25 c.c. of chloroform at  $21^{\circ}$  gave  $\alpha_D + 25'$ , corresponding to  $[\alpha]_D + 10.3^{\circ}$ .

*α-Benzoyl-α'-bromocamphor* was obtained in the following manner. One hundred grams of bromine were dissolved in an ice-cold aqueous solution containing 150 grams of potassium hydroxide, and slowly added to 20 grams of 1-hydroxy-2-benzoylcamphene dissolved in dilute potash. The sticky solid which immediately separated soon hardened, and after an interval of 12 hours was collected, washed, and recrystallised from boiling alcohol. The yield of *αα*-benzoylbromocamphor obtained by this method is quantitative, and the product consists chiefly of the variety of high melting point. It dissolves very readily in chloroform, but only sparingly in cold alcohol or benzene, and is almost insoluble in boiling light petroleum; it crystallises from hot alcohol in transparent, rectangular plates, begins to shrink and to change colour at about 190°, and melts at 214° to a pale brown liquid which evolves gas. The substance may be crystallised from concentrated nitric acid without undergoing change:

0.1353 gave 0.0756 AgBr. Br = 23.77.

$C_{17}H_{19}O_2Br$  requires Br = 23.88 per cent.

A solution containing 0.5015 gram in 25 c.c. of benzene at 21° gave  $\alpha_D - 2.8'$  in a 2 dcm. tube, whence the specific rotatory power  $[\alpha]_D - 53.2'$ ; 0.6451 gram dissolved in 25 c.c. of chloroform at 21° gave  $\alpha_D - 1.0'$ , corresponding to  $[\alpha]_D - 19.3'$ .

*Action of Alcoholic Potassium Hydroxide on αα-Benzoylbromocamphor.*—A specimen of *α*-benzoyl-*α'*-bromocamphor which melted at 210° and gave  $[\alpha]_D - 18.5'$  in chloroform, was heated during 4 hours in a reflux apparatus with potassium hydroxide (2 mola.) dissolved in alcohol. The liquid soon became dark brown, and on evaporation yielded a residue which dissolved completely in water. A current of well washed carbon dioxide was then passed into the aqueous solution until no further precipitation occurred, and the product, after crystallisation from alcohol, was obtained in the pink octahedra characteristic of 1-hydroxy-2-benzoylcamphene.

The same compound was obtained by reducing *α'*-benzoyl-*α*-bromocamphor with alcoholic potassium hydroxide.

*Action of Bromine on 1-Benzoxo-2-benzoylcamphene.*—When a solution of 1-benzoxo-2-benzoylcamphene in chloroform is treated with bromine, the colour of the halogen is not immediately destroyed, but after an interval, action is found to have taken place.

Ten grams of the dibenzoyl derivative were dissolved in 100 c.c. of chloroform and enclosed in a stoppered bottle with 4.4 grams (1 mol.) of bromine. After 24 hours, the colour of the halogen had almost disappeared. On allowing the liquid to evaporate, a considerable quantity of hydrogen bromide was liberated, and a crystalline residue was obtained having the odour of ethyl benzoate. The solid product,



weighing 9 grams, was exhausted with 50 c.c. of hot alcohol, and the solution deposited crystals melting at 110—115° and giving  $[\alpha]_D + 4.1^\circ$  in chloroform:

0.1598 gave 0.0884 AgBr. Br = 23.54.

$C_{17}H_{19}O_2Br$  requires Br = 23.88 per cent.

The substance was evidently a mixture of the two *aa*-benzoylbromocamphors, and by repeated crystallisation from alcohol, a specimen of the modification of higher melting point was obtained, giving  $[\alpha]_D - 19.5^\circ$  in chloroform.

*Conversion of One Isomeride into the Other.*—During the first attempt to separate the isomerides from one another by fractional crystallisation, a most unexpected change of the variety of lower melting point took place. A specimen of that substance, which had been recrystallised twice from alcohol without altering the melting point, melted at 111—112° and gave  $[\alpha]_D - 29.0^\circ$  in benzene; it was dissolved in hot alcohol, which on cooling deposited lustrous plates melting at 201—204°, and giving  $[\alpha]_D - 51.0^\circ$  in benzene. Although we have not succeeded in reproducing the conditions of this experiment, the transformation of one modification into the other can be effected by the agency of hydrogen bromide. A specimen of  $\alpha'$ -benzoyl- $\alpha$ -bromocamphor melting at 109—111° and giving  $[\alpha]_D + 2.9^\circ$  in chloroform was finely powdered and placed in a stoppered bottle with sufficient fuming hydrobromic acid to convert it into a thin paste. The following morning, water was added and the solid product filtered and washed. The substance, when dried in the desiccator, melted at about 200° and gave  $[\alpha]_D - 18.6^\circ$  in chloroform, and when recrystallised from alcohol yielded the lustrous plates characteristic of  $\alpha$ -benzoyl- $\alpha'$ -bromocamphor.

#### *Action of Bromine on $\alpha$ -Benzoylcamphor.*

In describing the  $\alpha$ -substituted halogen di-derivatives of camphor, Lowry (Trans., 1898, 73, 572) suggests that "the production of stereoisomeric di-derivatives is most readily explained by supposing that the action of the halogen involves addition to the enolic form of the mono-derivative." This explanation is a very probable one, and the following experiment appears to give it direct support.

A specimen of ketonic  $\alpha$ -benzoylcamphor, giving only a faint coloration with ferric chloride, was dissolved in cold glacial acetic acid containing sodium acetate ( $1\frac{1}{2}$  mols.); to this liquid, a solution of bromine (1 mol.) in glacial acetic acid was added, when it was observed that the colour of the halogen was immediately destroyed. Although it must be remembered that a small proportion of the benzoylcamphor is enolised by the solvent, it is still fair to say that the behaviour of  $\alpha$ -benzoylcamphor towards bromine exactly resembles that of the

unsaturated enolic isomeride, and it is noteworthy that the identity extends to the product of the change, which gives rise to  $\alpha'$ -benzoyl- $\alpha$ -bromocamphor in both cases.



Having found that potassium hypobromite converts 1-hydroxy-2-benzoylcamphene into a mixture of the benzoylbromocamphors, we employed the corresponding method in preparing the benzoylchlorocamphors in preference to treating the hydroxy-compound with the free halogen. Ten grams were dissolved in dilute aqueous potassium hydroxide, cooled with fragments of ice, and treated with 200 c.c. of a solution of sodium hypochlorite containing 30 grams of available chlorine per litre. A pink, dough-like solid separated and rapidly became hard. After an interval of several hours, the product was collected, washed, and extracted with 100 c.c. of boiling alcohol, thus dividing the substance into two portions, of which the more readily soluble melted somewhat indefinitely at  $85-87^\circ$  and gave  $[\alpha]_D -20.6^\circ$  in chloroform, whilst the residual fraction melted at  $219^\circ$  and gave  $[\alpha]_D +26.0^\circ$ .

$\alpha'$ -Benzoyl- $\alpha$ -chlorocamphor, obtained by recrystallising the more soluble fraction from alcohol and then from light petroleum, crystallises from each solvent in prisms and melts at  $88^\circ$ :

0.1284 gave 0.0627 AgCl. Cl = 12.08.

$C_{17}H_{19}O_2Cl$  requires Cl = 12.22 per cent.

It is readily soluble in alcohol and very freely so in chloroform, but dissolves only sparingly in light petroleum. A solution containing 0.4185 gram in 25 c.c. of chloroform at  $21^\circ$  gave  $\alpha_D -56'$  in a 2 dm. tube, whence the specific rotatory power  $[\alpha]_D -27.9^\circ$ .

$\alpha$ -Benzoyl- $\alpha'$ -chlorocamphor remains after the mixture of the two isomerides has been exhausted with a small quantity of hot alcohol; it crystallises from that solvent in plates resembling the corresponding bromo-derivative and melts at  $219^\circ$ :

0.1324 gave 0.0658 AgCl. Cl = 12.29.

$C_{17}H_{19}O_2Cl$  requires Cl = 12.22 per cent.

It is freely soluble in chloroform, but dissolves only sparingly in alcohol and is insoluble in light petroleum. A solution containing 0.3973 gram in 25 c.c. of chloroform at  $21^\circ$  gave  $\alpha_D +50'$  in a 2 dm. tube, whence the specific rotatory power  $[\alpha]_D +26.2^\circ$ .

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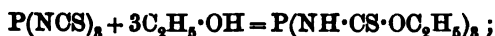
## XVII.—*The Action of Phosphorus Trithiocyanate on Alcohol.*

By AUGUSTUS EDWARD DIXON, M.D.

IN a preliminary note (*J. pr. Chem.*, 1872, [ii], 7, 474), Lössner records that he has obtained (1) by the action of phosphorus trichloride on potassium thiocyanate in alcoholic solution, a substance crystallising in fine needles, whose analysis leads to the empirical formula  $C_8H_{18}ON_4S_4$ ; and (2) from benzoyl chloride and alcoholic potassium thiocyanate, a compound,  $C_8H_9ONS$ . No analytical results are given in this note, which is very brief; but the interaction in which benzoyl chloride takes part is dealt with by Lössner at considerable length in a paper published a couple of years later (*ibid.*, 1874, [ii], 10, 237); the compound  $C_8H_9ONS$  now appears as  $C_{10}H_{11}O_2NS$ , that is, benzoyl thiocyanate *plus* a mol. of ethyl alcohol, and is regarded by him as 'benzoylethylloxysulphocarbamic acid,'  $PhCO \cdot NEt \cdot CO \cdot SH$ ; a paper dealing with the constitution of this substance and of certain of its derivatives has lately been published (Dixon, *Trans.*, 1899, 75, 375).

No reference is made in Lössner's second communication to the compound  $C_8H_{18}ON_4S_4$ ; nor, in fact, so far as the author can ascertain, is any description of it to be found in chemical literature. It is not easy to understand how a substance of this composition could be formed out of the materials used, unless through the occurrence of some profound decomposition; with the view of ascertaining whether such a change really took place, and more particularly since the interaction to be expected of these substances appeared to belong to the class of interactions recently studied by the writer, in which phosphorus and phosphoryl 'thiocyanates' take part (*Trans.*, 1901, 79, 541), it was decided to re-examine Lössner's reaction.

Before doing so, and incidentally to the incipient study just mentioned, some experiments were carried out in order to learn whether "phosphorus thiocyanate,"  $P(SCN)_3$  or  $P(NCS)_3$ , would unite directly with ethyl alcohol so as to afford a phosphoretted thiourethane, thus:



although, in view of the great ease with which both this and the corresponding phosphoryl derivative undergo hydrolysis, it scarcely seemed probable.

The phosphorus compound was prepared as already described (*loc. cit.*, p. 545), about 13 grams of phosphorus trichloride being used in each preparation: on treating the benzene solution with absolute

alcohol, there was marked evidence of chemical interaction, the temperature rising in three successive experiments in which it was measured, by  $47^{\circ}$ ,  $46^{\circ}$ , and  $59^{\circ}$  respectively, whilst free thiocyanic acid was evolved. On concentrating the mixture at the ordinary temperature, a yellow, crystalline solid was deposited; the mother liquor formed a clear brown syrup, intensely acid, reacting freely for thiocyanic acid and phosphorus, and soon beginning to decompose with evolution of mercaptan.

The solid product occurred in limited quantity, not more than a gram, at most, being obtained for every 13 grams of trichloride used; it was insoluble in benzene, sparingly soluble in boiling water, and moderately so in hot alcohol, but did not crystallise well from the latter solvent. When recrystallised from much boiling water, it was obtained in yellow, flexible, hair-like needles (on one occasion several inches long and closely resembling *Spirogyra* in outward appearance): they began to darken and change at about  $230^{\circ}$ , but were not melted at  $250^{\circ}$ .

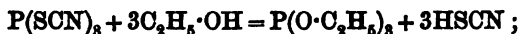
The substance contains no phosphorus, and hence is not the desired phosphorus trithiotriurethane. It is desulphurised by heating in alcoholic solution with ammoniacal silver nitrate, or with alkaline lead tartrate; its aqueous solution is somewhat acid to litmus and gives with lead acetate a bright yellow precipitate. Ferric chloride yields practically no colour reaction, either when added to the aqueous solution or to the mixture produced by first dissolving the solid in warm alkali hydroxide and then acidifying the solution with hydrochloric acid. The substance dissolves readily in potassium cyanide solution, and the resultant liquid, if acidified and treated with ferric chloride, now gives the intense blood-red thiocyanic reaction.

From the properties just described, there could be little doubt that the substance was nothing more than isopersulphocyanic acid,  $C_2H_2N_2S_3$ , and the results of analysis showed this to be the case:

S found, 64.3; N found, 18.9;

$C_2H_2N_2S_3$  requires S = 64; N = 18.7 per cent.

The mechanism whereby this substance comes to be formed is probably as follows: the "phosphorus thiocyanate" is decomposed in part by the alcohol, yielding free thiocyanic acid:



whilst another portion, in like manner, yields phosphorous acid: under the influence of this mineral acid, the former could afford isopersulphocyanic acid, thus:



Save the isopersulphocyanic acid, no other solid product was found;

consequently, if the phosphorus trithiotriurethane is formed, or, at all events, continues to exist, under the above conditions, it must be as one of the constituents of the acid, syrupy mother liquor, but the foul smell of the latter rendered it so unpleasant to work with that it was not examined further. However, as phosphorus trithiotriurethane, if capable of existence under ordinary circumstances, would probably be a solid substance more or less easily decomposable by moisture, it is doubtful whether it could have been extracted from the liquor, even if present.

As regards the interaction between alcoholic potassium thiocyanate and phosphorus trichloride, there was scarcely any reason to anticipate that it would run a course materially different from that between phosphorus trithiocyanate and alcohol; however, the experiment was tried, with the following result.

On dropping phosphorus trichloride into a saturated solution of potassium thiocyanate in 99.5 per cent. alcohol, violent action occurred, and potassium chloride was precipitated; on filtering this off and concentrating the filtrate by slow evaporation, thiocyanic acid escaped, and yellow, crystalline material separated in an oily, very acid, liquid; the former, when recrystallised from boiling water, proved to be identical with the solid obtained from phosphorus thiocyanate and alcohol, namely, *isopersulphocyanic acid*. In this case, as the liberated thiocyanic acid is in contact with much free hydrochloric acid proceeding from the interaction between the phosphorus haloid and the alcohol, it is a simple matter to account for the production of *isopersulphocyanic acid*. As in the preceding case, the quantity of this acid bears but a small proportion to the amount of phosphorus chloride used. So far, the writer has failed to identify any other substance in the solid product, yet Lössner, strange to say, does not mention the occurrence of *isopersulphocyanic acid* at all.

It would seem, therefore, either that the interaction must have proceeded on different lines when conducted by this chemist, or else that, through some accident, he must have attributed to *isopersulphocyanic acid*,  $C_2H_2N_2S_2$ , the formula  $C_8H_{18}ON_4S_4$ . How this could happen it is not very easy to see, considering that the percentages of sulphur are 64 and 40.8, respectively. It is conceivable, however, that some unsuspected cause of error may have temporarily crept into his analytical practice, more especially bearing in mind that his benzoyl chloride product, above mentioned, which was stated in the preliminary note to have, according to the results of analysis, the formula  $C_8H_7ONS$ , turns out to be really  $C_{10}H_{11}O_2NS$ ; here the theoretical results are by no means so widely divergent as in the preceding case, but still the figures differ by nearly 4 per cent. for the sulphur, 3 per cent. for the nitrogen, and so on.

In the hope of possibly obtaining phosphorus tribenzyltrithiocarbamate, a cold, somewhat dilute solution of "phosphorus thiocyanate" in benzene was treated with benzyl alcohol. Interaction occurred at once, the temperature of the mixture rising by about 30°; but after driving off the solvent and allowing the residue to stand, a mere trace of white, solid matter was deposited, the amount being too small to permit of identification. It crystallised well in white prisms from boiling water, volatilised completely, on heating, without preliminary fusion, gave no ammonia when heated with alkali, contained no phosphorus, gave no colour reaction with potassium cyanide, hydrochloric acid, and ferric chloride, and consequently was neither isopersulphocyanic acid nor phosphorus tribenzyltrithiocarbamate. The mother liquor was almost completely volatile in a current of steam; the distillate, a yellowish oil, consisted partly of unchanged benzyl alcohol, and partly of an unpleasant smelling oil which contained sulphur but no phosphorus, the latter being wholly retained in the trifling residue of the steam distillation.

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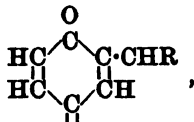
### XVIII.—*The Relationship between the Orientation of Substituents in and the Constitution of Benzeneazo- $\alpha$ -naphthol.*

JOHN THEODORE HEWITT and SAMUEL JAMES MANSON AULD.

THE question of the constitution of the oxyazo-compounds has aroused a considerable amount of discussion, and in order to obtain further information on this point, one of the authors of the present communication has, in conjunction with several of his pupils, made experiments on the substitution derivatives of these substances. In all cases so far studied, the results have given an unqualified support to the oxyazo-formula, the phenolic nucleus always being first attacked by dilute nitric acid or bromine in presence of an excess of sodium acetate. The appearance of a communication by Möhlau and Kegel (*Ber.*, 1900, 33, 2858), in which they ascribed a tautomeric formula to benzeneazo- $\alpha$ -naphthol, rendered necessary the further investigation of the action of substituting agents on the benzeneazonaphthols. The results obtained in the case of the azo-derivatives of  $\beta$ -naphthol are reserved for a future communication.

Möhlau and Kegel found that *p*-quinones and their derivatives

generally reacted with benzhydrol and Michler's hydrol (tetramethyldiaminobenzhydrol) to form compounds of the type  $[R = C_6H_5 \text{ or } C_6H_4 \cdot N(CH_3)_2]$ :



and extending the reaction to the so-called benzeneazo- $\alpha$ -naphthol obtained substances in which the hydrol had behaved as if the azo-compound were quinonoid in type. Had a strong acid been present, such a reaction would not have been surprising; the condensation was, however, carried out in the absence of such a compound. Moreover, the complicated azo-derivatives so obtained behaved, on acetylation, as quinone-hydrazones, the acetyl group attaching itself to a nitrogen atom. By the complete reduction of the acetyl derivative of benzeneazotetramethyldiaminobenzhydrol- $\alpha$ -naphthol, Möhlau and Kegel obtained acetanilide but could detect no aniline; from these results, they concluded that benzeneazo- $\alpha$ -naphthol, as well as the condensation product with Michler's hydrol, had the constitution of quinone-hydrazones. The condensation was, however, not incompatible with the presence of both forms in equilibrium in solution, whilst the course of the acetylation of the condensation product might be explained in a similar way in conjunction with the undoubted steric hindrance which might be experienced in the case of acetylating an ortho-substituted  $\alpha$ -naphthol. We therefore resolved to re-examine the acetylation of benzeneazo- $\alpha$ -naphthol, and further to study the action of substituting agents on the azo-naphthol itself. It may be mentioned here that the results of all experiments made with nitric acid on benzeneazo- $\alpha$ -naphthol were thoroughly unsatisfactory; either reaction did not take place or only tarry products were obtained.

#### *Reduction of Benzeneazo- $\alpha$ -naphthyl Acetate.*

Benzeneazo- $\alpha$ -naphthol was prepared by Witt and Dedichen's method (*Ber.*, 1897, 30, 2657), and acetylated by boiling in a reflux apparatus with excess of acetic anhydride and fused sodium acetate. The melting point of the product ( $128^\circ$ ) agreed with that given by Zincke and Bindewald (*Ber.*, 1884, 17, 3030). The complete reduction of this substance was effected in cold alcoholic solution, so that any possibility of one or other product becoming acetylated during the process and thus leading to erroneous conclusions might be obviated. Two grams of the acetyl derivative were dissolved in 100 c.c. of absolute alcohol and treated with 5 c.c. of concentrated sulphuric acid mixed with 10 c.c. of alcohol. Zinc dust was now added and the solution well

shaken until entirely colourless. The excess of zinc dust was removed by filtration and the filtrate diluted with water, rendered alkaline with sodium carbonate, and then twice extracted with ether. The ethereal extracts were united, the excess of ether evaporated, and the residue distilled in a current of steam. The presence of aniline in the distillate was confirmed by its conversion into tribromoaniline. In one experiment, the weight of tribromoaniline obtained was practically equal to that of the benzeneazonaphthyl acetate employed. After the steam distillation, the residue in the flask was examined in order to isolate the other product of fission; the acetoxy- $\alpha$ -naphthylamine could not, however, be obtained in a crystalline form.

By partial reduction of benzeneazo- $\alpha$ -naphthyl acetate, a hydrazo-compound is obtained, which, from its insolubility in dilute alkali, evidently does not contain a free hydroxyl group. To obtain this substance, 1 gram of benzeneazo- $\alpha$ -naphthyl acetate was dissolved in alcohol, a small quantity of acetic acid added, and the solution shaken with zinc dust until colourless. The filtered solution deposited crystals on standing, which were collected, washed, and dried. The substance so obtained, although at first colourless, turned faintly yellow on drying; the melting point ( $160-165^\circ$ ) was far from sharp and the substance reddened considerably on heating.

0.1685 gave 0.4580  $\text{CO}_2$  and 0.0866  $\text{H}_2\text{O}$ . C = 74.13; H = 5.69.

0.1445 „ 11.9 c.c. nitrogen\* at  $15^\circ$  and 754 mm. N = 9.51.

$\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2$  requires C = 73.97; H = 5.48; N = 9.52 per cent.

These results absolutely confirm the constitution usually assigned to benzeneazo- $\alpha$ -naphthyl acetate, namely, that it is an oxygen ester.

The possibility of the existence of an isomeric derivative was also examined. Benzeneazo- $\alpha$ -naphthol, on treatment with mineral acids, readily furnishes salts of  $\alpha$ -naphthaquinone phenylhydrazone. Two grams of benzeneazo- $\alpha$ -naphthol were added to glacial acetic acid which had been saturated with hydrogen chloride and warmed in a flask provided with a reflux tube down which 8 grams of acetyl chloride were added in small quantities at a time. After half-an-hour's heating at  $100^\circ$ , the product was poured into water, the precipitate collected, and recrystallised from glacial acetic acid. The acetyl derivative so obtained melted at  $127^\circ$  and when mixed with the acetyl derivative prepared by acetylation with acetic anhydride and fused sodium acetate did not depress its melting point. Hence salts of  $\alpha$ -naphthaquinone phenylhydrazone furnished derivatives of benzeneazo- $\alpha$ -naphthol on acetylation.

\* Measured over 50 per cent. potassium hydroxide solution.



*Action of Bromine on Benzeneazo- $\alpha$ -naphthol.*

In acting with bromine on an oxyazo-compound, a solution or suspension of the latter in acetic acid is best employed, and it is very necessary to take especial care that hydrogen bromide is removed as quickly as it is formed. If this be not done, the hydrogen bromide converts oxyazo-compounds into salts of quinone-hydrazones and substitution takes place in the nucleus free from oxygen (Hewitt and Aston, *Trans.*, 1900, 77, 712, 810). The bromination of benzeneazo- $\alpha$ -naphthol has already been effected by Margary (*Gazzetta*, 1884, 14, 271), who took no precautions to avoid presence of a mineral acid. The substance so prepared he regarded as *p*-bromobenzeneazo- $\alpha$ -naphthol, stating that he obtained *p*-bromoaniline on reduction. Such a result would not have been surprising were it not that the product is described as occurring in two forms melting at 185° and 197° respectively, whereas the substance obtained synthetically by Bamberger melted at 237—238° (*Ber.*, 1895, 28, 1896).

Bromination, if carried out in the following manner, furnishes a product, melting at 196° which contains no bromine in the benzene nucleus. Benzeneazo- $\alpha$ -naphthol, together with its own weight of fused sodium acetate, is dissolved in 10 times its weight of glacial acetic acid. The calculated quantity of bromine, diluted with twice its weight of acetic acid, is then added and the mixture allowed to stand at the ordinary temperature in a closed flask until the odour of the bromine has disappeared; this frequently requires a week. The solid matter is then filtered off, washed with water, and recrystallised from boiling glacial acetic acid, in which the substance is fairly soluble, although the cold solvent dissolves it but sparingly. Analysis showed that a monobromo-derivative had been produced:

0.2040 gave 0.1132 AgBr. Br = 23.97.

0.2460 „ 0.1404 AgBr. Br = 24.22.

0.2239 „ 17.0 c.c. nitrogen at 20° and 737 mm. N = 8.61.

$C_{16}H_{11}ON_2Br$  requires Br = 24.42; N = 8.58 per cent.

The substance dissolves very easily in acetone, it is also dissolved by alcohol, ether, carbon disulphide, or ethyl acetate, benzene dissolves it only sparingly, whilst in light petroleum it is almost insoluble. The solution in strong sulphuric acid has a much bluer shade than that of the parent substance.

The reduction was effected by solution in alcohol and boiling with an excess of tin and hydrochloric acid in a reflux apparatus for 1 hour. After cooling, sodium hydroxide was added in excess and the mixture distilled in a current of steam. The distillate was rendered alkaline with soda, shaken with a small quantity of benzoyl chloride, and the

precipitate collected and recrystallised from benzene. Colourless plates separated, which proved to be free from halogen and melted at  $158^{\circ}$  (uncorr.). The substance was therefore benzanilide. It follows that when benzeneazo- $\alpha$ -naphthol is brominated in presence of sodium acetate, one atom of bromine enters the naphthol nucleus. The only benzeneazobromo- $\alpha$ -naphthol hitherto described is the 8-bromo-4-benzeneazo- $\alpha$ -naphthol prepared by Meldola and Streatfeild (*Trans.*, 1893, 63, 1058). It is probably not identical with our compound, although its melting point,  $197^{\circ}$ , lies very near to that of the substance obtained by direct bromination. To further characterise the latter, a number of derivatives have been prepared and analysed.

The *ethyl ether* was obtained by dissolving, successively, 0.1 gram of sodium and 1.0 gram of the azo-compound in 6 c.c. of ethyl alcohol and heating with an excess of ethyl bromide for 2 hours at  $120$ — $130^{\circ}$ . The precipitate obtained on addition of water was recrystallised twice from a mixture of chloroform and alcohol; the product melted at  $220^{\circ}$  (uncorr.):

0.1060 gave 0.0540 AgBr. Br = 22.51.

$C_{18}H_{16}ON_2Br$  requires Br = 22.53 per cent.

The ethyl ether is a black powder, fairly soluble in acetic acid and somewhat readily so in chloroform. Most of the other usual organic solvents dissolve it only sparingly in the cold.

The *acetyl* derivative was obtained by boiling in a reflux apparatus for 2 hours a mixture of the azophenol with  $1\frac{1}{2}$  times its weight of fused sodium acetate and 3 times its weight of acetic anhydride. The substance was isolated in the usual manner and recrystallised from glacial acetic acid; its melting point was found to be  $146^{\circ}$  (corr.):

0.1441 gave 8.55 c.c. nitrogen at  $8^{\circ}$  and 755 mm. N = 7.63.

$C_{18}H_{13}O_2N_2Br$  requires N = 7.59 per cent.

To compare the product obtained by substituting bromine in benzeneazo- $\alpha$ -naphthol with the three bromobenzeneazo- $\alpha$ -naphthols, the latter were prepared and converted into acetyl derivatives.

#### *The Isomeric Bromobenzeneazo- $\alpha$ -naphthols.*

*o*-Bromobenzeneazo- $\alpha$ -naphthol.—Pure *o*-bromoaniline (prepared from *o*-nitraniline by Sandmeyer's reaction and subsequent reduction of the *o*-bromonitrobenzene so obtained) was diazotised, the solution of the diazonium salt added to the requisite quantity of  $\alpha$ -naphthol dissolved in methylated spirit, and an aqueous solution of sodium acetate stirred into the mixture. The product was collected, washed with dilute alcohol, and recrystallised from glacial acetic acid, in which it is fairly

soluble on boiling, but only sparingly so when cold. It melted at  $183^{\circ}$  (corr.):

0.2917 gave 21.0 c.c. nitrogen at  $14^{\circ}$  and 754 mm.  $N = 8.49$ .

$C_{16}H_{11}ON_2Br$  requires  $N = 8.58$  per cent.

The *acetyl* derivative, after recrystallisation from boiling glacial acetic acid, melted at  $123^{\circ}$ :

0.1728 gave 10.3 c.c. nitrogen at  $14^{\circ}$  and 754 mm.  $N = 7.03$ .

$C_{18}H_{15}O_2N_2Br$  requires  $N = 7.59$  per cent.

*m*-Bromobenzeneazo- $\alpha$ -naphthol, after recrystallisation from benzene, melted at  $211^{\circ}$  (uncorr.):

0.2298 gave 16.8 c.c. nitrogen at  $20^{\circ}$  and 761 mm.  $N = 8.36$ .

$C_{16}H_{11}ON_2Br$  requires  $N = 8.58$  per cent.

The *acetyl* derivative was prepared in the usual manner; it melted at  $112^{\circ}$ :

0.1252 gave 9.0 c.c. nitrogen at  $23^{\circ}$  and 744 mm.  $N = 7.80$ .

$C_{18}H_{15}O_2N_2Br$  requires  $N = 7.59$  per cent.

*p*-Bromobenzeneazo- $\alpha$ -naphthol has already been described by Bamberger (*Ber.*, 1895, 28, 1896). The melting point given by him is  $237-238^{\circ}$ ; our preparation melted at  $226^{\circ}$  (uncorr., the corrected melting point would be about  $233^{\circ}$ ). These melting points do not differ materially, but are far removed from those given by Margary, namely,  $185^{\circ}$  and  $197^{\circ}$  (*loc. cit.*). On analysis:

0.0572 gave 0.0328 AgBr.  $Br = 24.36$ .

$C_{16}H_{11}ON_2Br$  requires  $Br = 24.42$  per cent.

The *acetyl* derivative was also prepared in order to characterise the substance further. Prepared in the usual manner and recrystallised from glacial acetic acid, it melted at  $141^{\circ}$  (corr.):

0.1484 gave 0.3195  $CO_2$  and 0.0499  $H_2O$ .  $C = 58.72$ ;  $H = 3.68$ .

$C_{18}H_{15}O_2N_2Br$  requires  $C = 58.54$ ;  $H = 3.52$  per cent.

The substance is easily soluble in benzene or chloroform, fairly so in acetone or ethyl acetate, but only sparingly so in alcohol.

It is thus conclusively proved that in absence of strong acids, benzeneazo- $\alpha$ -naphthol furnishes a substance which does not contain bromine in the benzene nucleus. The position of the bromine atom in the  $\alpha$ -naphthol nucleus has not been determined; it probably enters position 2. So far, attempts at preparing the substance by the interaction of phenylhydrazine and Zincke and Schmidt's 2-bromo-1:4-naphthaquinone (*Ber.*, 1894, 27, 2757) have been unsuccessful, although from the production of benzeneazo- $\alpha$ -naphthol from  $\alpha$ -naphtha-

quinone and phenylhydrazine observed by Zincke and Bindewald, the carrying out of such a reaction appears easy of accomplishment. Under the circumstances, we are compelled to leave the actual proof that position 2 is occupied by the bromine atom to some future occasion.

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## XIX.—*The Magnetic Rotation of some Polyhydric Alcohols, Hexoses, and Saccharobioses.*

By W. H. PERKIN, sen., Ph.D., F.R.S.

THE remarkable changes in optical activity which many carbohydrates show when in solution in water have engaged the attention of several observers for a long period. To take an example, a freshly prepared solution of glucose has a rotation of  $[\alpha]_D +105.16^\circ$ , but this gradually diminishes and finally becomes constant after about six hours, the rotation being then  $[\alpha]_D +52.49^\circ$  (Parcus and Tollens, *Annalen*, 1890, 257, 160). This phenomenon has been called bi-, multi-, or muta-rotation, and it has been suggested by Tanret (*Compt. rend.*, 1895, 120, 1060) that the first form of glucose should be called  $\alpha$ -glucose and the second  $\beta$ -glucose; this method of distinguishing the two modifications will be used in the present paper, not only in the case of glucose, but in all cases where birotation has been observed.

A résumé of the views which have been entertained in reference to birotation is given in a paper by Horace Brown and S. U. Pickering "On the thermal changes attending change of rotatory power of carbohydrates" (*Trans.*, 1897, 71, 769). From this, it is seen that the earlier attempts to explain the phenomenon of bi- or multi-rotation were based on physical considerations. Subsequently, the probable chemical aspect of the matter came to be more fully discussed; E. Fischer, for example, has suggested that the remarkable birotation shown by glucose may be due to the gradual assimilation of water and conversion into the heptahydric alcohol,  $C_6H_{14}O_7$ . This view has latterly found considerable favour, and Brown and Pickering think that the results of the heat determinations made by them are consistent with it.

As the study of the magnetic rotations of the sugars might possibly throw some light on this difficult subject, it was thought desirable to undertake the examination of some of the more important of these substances. Until lately, however, the measurements could not be

made with any degree of accuracy, because strong solutions of these sugars rotate the plane of polarisation through such large angles that, as is well known, the impurities in the sodium light seriously affect the appearance of the half-shadow disc of the polarimeter, causing the two sides to be very unequally tinted, so that useful numbers cannot be obtained. Thus, a 50 per cent. solution of fructose in a 100 mm. tube has an optical rotation of about  $50^\circ$ , and this is the point at which the magnetic rotation commences. Fortunately, after many attempts, I have succeeded in finding a simple spectroscopic arrangement by which this difficulty can be overcome, so that very large angles may now be measured with considerable accuracy, and with this new arrangement I have found it possible to determine accurately the magnetic rotations of a number of carbohydrates. In a future communication, I hope to give an account of this improvement and also of the new apparatus which I am at present using for the determination of magnetic rotations.

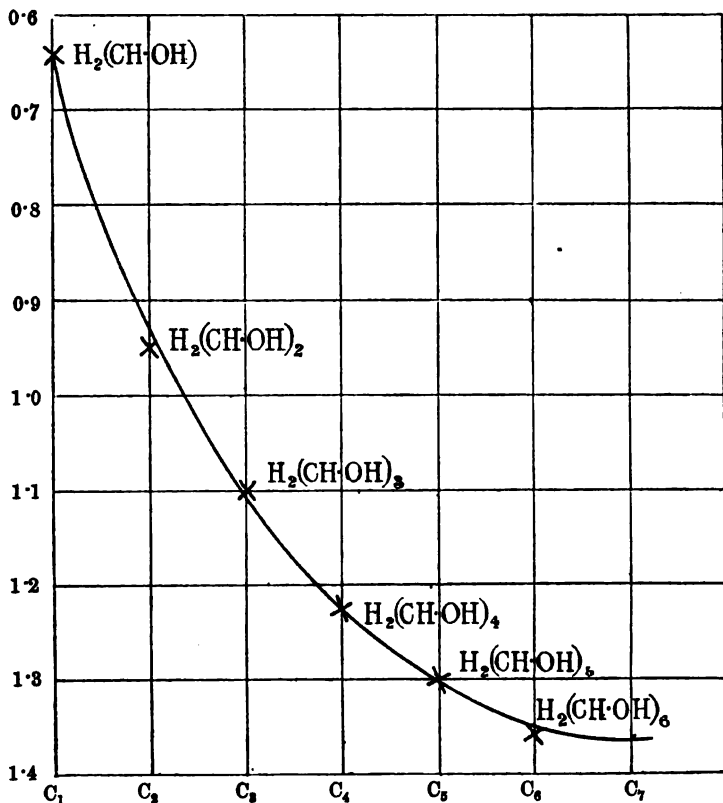
Besides the sugars themselves, two of the polyhydric alcohols have been measured, so that the magnetic rotations of this class of compounds from the mono- to the hexa-hydric are now known, with the exception of that of the pentahydric alcohol,  $C_5H_{12}O_5$ , which, however, can be easily estimated. The examination of this series of alcohols was important in order that a basis might be obtained from which to calculate the probable rotation of the various sugars.

The numbers obtained for the magnetic rotation of this group of alcohols may be briefly summarised as follows :

		Mol. mag. rot.
Methyl alcohol.....	$H_2(CH\cdot OH)$	1.640
Glycol .....	$H_2(CH\cdot OH)_2$	2.943
Glycerol .....	$H_2(CH\cdot OH)_3$	4.111
Erythritol .....	$H_2(CH\cdot OH)_4$	5.230
Pentitol (missing) .....	$H_2(CH\cdot OH)_5$	6.300 est.
Mannitol .....	$H_2(CH\cdot OH)_6$	7.351

If the magnetic rotations of the alcohols actually examined be plotted out, they form a regular curve, from which the rotation of the missing pentahydric compound may be calculated; also if the curve be carried further, the rotations of the heptahydric and other higher alcohols may be estimated, doubtless with considerable accuracy (see diagram). From this curve, it will be at once seen that the successive  $CH\cdot OH$  groups have a smaller and smaller value as they are repeated; this, however, is not due to the group  $CH\cdot OH$  as a whole, but to the hydroxyl group which it contains, since in the homologous series of paraffins, aliphatic acids, monohydric alcohols, and esters, it has been conclusively proved that the value of each  $CH_2$ , even in compounds containing eighteen carbon atoms, is constant, namely, 1.023.

Attention has previously been directed to the diminishing influence caused by successive displacements of hydrogen by hydroxyl (Trans., 1884, 45, 559); this diminishing influence is more clearly seen by subtracting from the value of the polyhydric alcohol that of the corresponding alcohol containing one hydroxyl less in its molecule. In these cases, in which the magnetic rotation of the latter has not been



The magnetic rotations are found by adding the ordinates to the carbon numbers of the abscissae.

directly determined, it can be obtained by the addition of the value of CH<sub>2</sub> to that of the next lower alcohol, thus :

		Mol. mag. rot.	Diff. for OH disp. H.
Glycol .....	C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub>	2.943	0.163
Ethyl alcohol ...	C <sub>2</sub> H <sub>5</sub> (OH)	2.780	
Glycerol .....	C <sub>3</sub> H <sub>5</sub> (OH) <sub>3</sub>	4.111	0.145
Less .....	CH <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub>	3.966	

		Mol. mag. rot.	Diff. for OH disp. H.
Erythritol .....	$C_4H_6(OH)_4$	5.230	0.096
Less .....	$CH_2 + C_3H_5(OH)_3$	5.134	
Pentitol .....	$C_5H_7(OH)_5$	6.300	0.047
Less .....	$CH_2 + C_4H_6(OH)_4$	6.253	
Mannitol .....	$C_6H_8(OH)_6$	7.351	0.028
Less .....	$CH_2 + C_5H_7(OH)_5$	7.323	

The influence of the hydroxyl group displacing hydrogen must, therefore, evidently become practically *nil* when the substitution has been repeated seven or eight times. The results exhibited in the above tables will be found to be very important in the calculation of the probable rotations of glucose, fructose, &c.

Glucose is known to be an aldehyde. Now the difference between the molecular magnetic rotations of an aldehyde and an alcohol, for example, between those of heptyl alcohol and heptyl aldehyde, is 0.438, so that the calculated rotation of glucose can be obtained by subtracting this amount from that of mannitol.\*

Mannitol .....	7.351
Less .....	0.438
Glucose .....	6.913

Fructose is known to be a ketone. The difference between the magnetic rotation of a ketone and an alcohol, for example, between that of *sec.*octyl alcohol and of methyl hexyl ketone, is 0.495; this subtracted from the value for mannitol should give the rotation of fructose.

Mannitol .....	7.351
Less .....	0.495
Fructose.....	6.856

The actual determinations of the magnetic rotations of glucose and fructose in aqueous solution have given almost identical numbers in both cases, but the results are considerably lower than those calculated above.

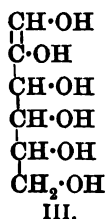
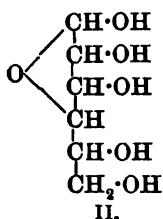
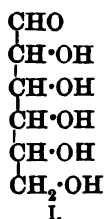
Glucose calc.....	6.913	Fructose calc.....	6.855
Found .....	6.723	Found.....	6.729
Diff. ....	0.190	Diff.....	0.126

\* The actual comparison should, of course, be between glucose and sorbitol, but the change of one asymmetric carbon atom in passing from sorbitol to mannitol would have, if any, so little effect on the magnetic rotation that it may be neglected.

The question then arises : Why are the actual magnetic rotations of these sugars, determined in solutions which have undergone the usual maximum change in optical rotation, lower than those calculated ? Is this due to the assimilation of water and the formation of a heptahydric alcohol,  $C_6H_7(OH)_7$ , or must some other explanation be found ?

From the experimental part of the paper, it is seen that the magnetic rotation of glucose in aqueous solution, obtained by subtracting the value of  $11H_2O$  from that of a solution of the composition  $C_6H_{12}O_6 \cdot 11H_2O$ , is found to be 6.723, and the same number is found in a similar way from solutions of other concentrations. If, however, the glucose had assimilated 1 mol. of water from the solution to form the heptahydric alcohol  $C_6H_7(OH)_7$ , the rotation of this compound will be obtained by subtracting the value of only  $10H_2O$  from the result of the determination, that is to say, it will be 7.723. From the examination of the curve (p. 179), it is clear that the rotation of the alcohol  $C_7H_8(OH)_7$  will be 8.380 ; if from this we deduct the value for  $CH_2$  (1.023), we obtain 7.347 as the value of the alcohol  $C_6H_7(OH)_7$ , a number which is very different from that actually found, namely, 7.723. This evidence therefore seems to show that glucose in solution is the anhydrous substance  $C_6H_{12}O_6$ , and is not combined with water to form the heptahydric alcohol  $C_6H_7(OH)_7$ .

Lowry (Trans., 1899, 75, 215), when referring to the subject of birotation, suggests that the difference between glucose in the anhydrous condition and in solution, after all change has taken place and the optical rotation become constant, may be due simply to *isomeric* change, the aldehydic form I in the following table passing partly into one of the isomeric modifications II or III. Of these expressions, formula II was first proposed by Tollens (*Ber.*, 1883, 16, 923), and afterwards considered by E. Fischer as possibly, although not probably, representing the constitution of anhydrous glucose.



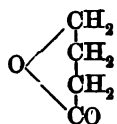
If, however, formula III be examined, it will be seen that it represents an unsaturated compound, and this, according to the magnetic rotation, cannot be correct. The introduction of an ethylene linking into the molecule of a saturated substance is known to raise



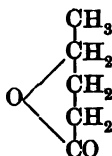
the magnetic rotation by  $1.620^*$ , and the value of glucose (calculated from mannitol) would thus become  $6.913 + 1.620 = 8.533$ , which is far higher than the value actually found ( $6.723$ ).

It has already been pointed out (p. 180) that the value for glucose in solution ( $6.723$ ) is lower by  $0.190$  than it should be if the substance were an aldehyde, and the question then arises whether a compound of the formula II would have a lower rotation than one having the aldehydic formula I. That this will be the case can be shown from the following comparisons between the values found for glucose in solution, and those of ethylene oxide and the lactones, that is, of substances which are constituted somewhat similarly to formula II.

The value of ethylene oxide  $\text{O} \begin{smallmatrix} \diagup \text{CH}_2 \\ \diagdown \text{CH}_2 \end{smallmatrix}$ , calculated from that of glycol ( $2.943$ ) by taking away  $0.751$  for the loss of the elements of water (see p. 184) is  $2.192$ , the value found was  $1.935$ , making a difference of  $0.247$  (Trans., 1893, 63, 490). In the case of the lactones which have been examined, namely, butyrolactone and valerolactone,



Butyrolactone.

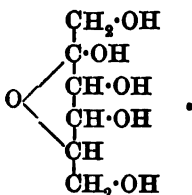


Valerolactone.

the following are the differences between values found and calculated in a similar way: for butyrolactone  $-0.230$ , and for valerolactone  $-0.195$ , average,  $0.212$ . Now the constitution represented by formula II agrees best with that of the lactones, inasmuch as it contains a chain of four carbon atoms closed by oxygen. If then glucose, when dissolved in water, assumes to a greater or less extent this constitution, there is good reason for believing that its rotation would be lower than that of the aldehydic form, I, by about  $0.2$ . This, it will be seen, agrees nearly exactly with the number actually found, and there is therefore strong support for the contention that, in solution, glucose has the constitution represented by formula II, or exists in some form analogous to this. The solution would probably also contain a small quantity of glucose in its ordinary aldehydic condition; it is therefore possible that the rotation of the  $\beta$ -form in the pure state may be a little lower still than that found.

\* The value for ordinary unsaturation with loss of  $\text{H}_2$  is  $1.112$ , but as no hydrogen is lost in this case, the value for unsaturation will be  $1.112 + 0.508$ , the value of  $\text{H}_2$ .

If now formula II be slightly modified, an expression for the possible condition of fructose in solution may, in a similar way, be obtained which will be as follows :



What has been said about glucose applies equally well to fructose ; the rotation is in both cases the same, and is lower than the calculated value, although not quite to the same extent ; it is therefore probable that fructose exists in solution, not as a ketone, but chiefly in a state represented by the above formula, or by some other formula similar to this.

If we now consider the relationship between the calculated magnetic rotation for glucose in its aldehydic form and that found for galactose in solution, we have the following numbers :

Glucose, calc. ....	6.913
Galactose, found .....	6.887
	<hr/>
	0.026

In considering these numbers, it should be noted that in optically active compounds, difference in configuration only does not appear to influence magnetic rotation ; it is therefore probable that the magnetic rotation of galactose as an aldehyde is the same as that of glucose as an aldehyde. If, then, galactose in aqueous solution had been present entirely in its aldehydic form, the number found should have been 6.913, and the slight lowering observed in the value, namely, 0.026, appears to show that, whilst present for the most part in its aldehydic form, galactose has to some extent been converted into a modification similar to that represented by formula II in the case of glucose in solution. It is, however, remarkable that this small change appears to be accompanied by so large an alteration in the optical rotation, since galactose, which shows a rotation of approximately  $[\alpha]_D + 134.5^\circ$  in freshly prepared solutions, has a value of only  $[\alpha]_D + 84.2^\circ$ , when the solution has been left to stand until the rotation has become constant, the formation of the small amount of the substance of formula II being accompanied by a fall in the optical rotation of no less than  $50.3^\circ$ . There is, however, no evidence to show what the optical rotation of substances of the type represented by formula II would be in the case of glucose,

fructose, or galactose. It is quite possible that such forms of the sugars, although similar in general character, might have very widely different optical rotations, and this is evidently the case, since fructose is laevorotatory in solution, whilst glucose and galactose are dextrorotatory in different degrees. Quite possibly a dextrorotatory aldehydic sugar might yield a laevorotatory substance of the type represented by formula II on going into solution, and this might be so in the case of galactose when it is entirely converted into its isomeric form. We have in nitrocamphor a remarkable instance of this kind of change, only of the reverse order;  $\alpha$ -nitrocamphor, which is laevorotatory, when changed into the isomeric  $\psi$ -nitrocamphor, becoming enormously dextrorotatory. Again,  $\pi$ -bromonitrocamphor in its normal condition has a rotation of  $[\alpha]_D -38^\circ$ , but in its pseudo-form has  $[\alpha]_D +188^\circ$  (Lowry, *Trans.*, 1899, 75, 223).

The birotation of galactose is also much increased in amount by the addition of lead acetate to its solution, the rotation falling by 53 per cent. (Hanno Svoboda, *Zeit. Ver. Rubenzucker.-Ind. Deut. Reichs*, 1896, 46, *Heft.* 481, 29 pages; also *Abstr.*, 1896, i, 406) I find also that a cold solution of caustic alkali reduces the rotation very considerably.

As sucrose represents glucose and fructose less 1 mol. of water, its magnetic rotation can be easily calculated.

The decrease in magnetic rotation caused by the loss of the elements of water when alcohol is converted into ethyl ether, acetic and propionic acids into their anhydrides, &c., averages about 0.752 (*Trans.*, 1886, 49, 787), being in some cases a little less, and in others a little more than this; therefore when this value is subtracted from those of the two sugars, the difference should approximately give the magnetic rotation of sucrose thus:

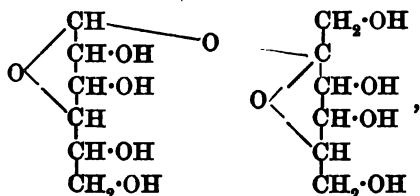
$\alpha$ -Glucose + $\alpha$ -fructose, calc.....	13.768
less $H_2O$ .....	0.752
	<hr/>
Sucrose calc. ....	13.016
found.....	12.586
	<hr/>
	- 0.430

From this it is seen that the experimental number is very much lower than the calculated. If, however, the experimental numbers of glucose and fructose in solution as  $\beta$ -modifications be taken instead of those calculated for the magnetic rotation of the anhydrous or  $\alpha$ -sugars, the following result is obtained:

$\beta$ -Glucose + $\beta$ -fructose found	.....13.452
less $H_2O$ .....	0.752
	<hr/>
Sucrose .....	12.700
found .....	12.586
	<hr/>
	- 0.114

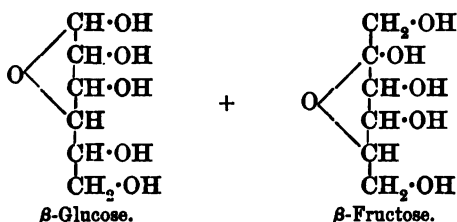
As the difference between the numbers actually found and those calculated in the above way is so small,\* it would seem that sucrose is apparently built up of the isomeric or  $\beta$ -forms of glucose and fructose, and not of the aldehydic and ketonic forms.

If, then, sucrose is built up of the isomeric forms of glucose and fructose, it will probably have the formula :



and its constitution in the dry state and in solution will most likely be the same, since it does not exhibit the phenomenon of birotation.

The above formula for sucrose has already been proposed by E. Fischer (*Ber.*, 1893, 26, 2405); it is a modification of that suggested by Tollens (*Ber.*, 1883, 16, 923), and clearly shows that when sucrose is hydrolysed it should at first be resolved into the isomeric or  $\beta$ -modifications of glucose and fructose :

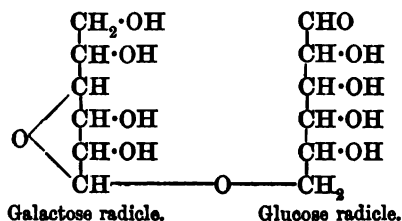


### *Maltose and Lactose.*

These sugars differ in a marked manner from sucrose in that they possess birotatory and cupric reducing powers ; there can therefore be no doubt that they must have a structure essentially different from that of sucrose.

\* If, as supposed, the numbers found for these  $\beta$ -compounds are a trifle high, on account of the solution containing a little of the  $\alpha$ -compounds (see p. 182), this difference would be still smaller.

In order to account for this difference, E. Fischer (*loc. cit.*) suggests the following formula for lactose:



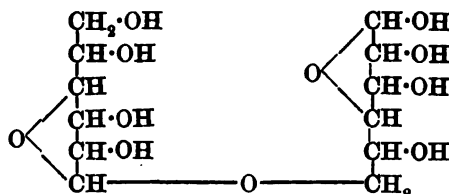
In this, the galactose radicle is represented as in the  $\beta$ - and the glucose radicle in the  $\alpha$ -condition, whilst if this formula be applied to maltose, one glucose radicle will be in the  $\beta$ - and the other in the  $\alpha$ -condition. On investigating this matter, it was at first thought that the view of the difference in constitution between maltose and lactose on the one hand, and of sucrose on the other, received some immediate confirmation from the results of the magnetic rotations of the former, which are rather higher than the value obtained for sucrose; no doubt this has a bearing on the subject, but it is doubtful whether any great importance can be attached to this difference. From the fact, however, that these carbohydrates contain a glucose instead of a fructose radicle, their magnetic rotations should be about 0.057 higher than that of sucrose. The rotations are as follows:

Maltose, found	.....	12.690
Sucrose	„	.....12.586
		<hr/>
		+ 0.104
Lactose, found	.....	12.714
Sucrose	„	.....12.586
		<hr/>
		+ 0.128

If maltose be first considered, its magnetic rotation, on the assumption that its constitution is represented by the above formula, may be calculated thus:

$\beta$ -Glucose, found	.....	6.723
$\alpha$ -Glucose, calc.	.....	6.913
		<hr/>
		13.636
Less $\text{H}_2\text{O}$ .....		0.752
		<hr/>
Calculated mol. mag. rot. of maltose...		12.884
Found.....		12.690
		<hr/>
Diff.....		0.194

This difference is almost exactly the same as that observed between  $\alpha$ -glucose and  $\beta$ -glucose, 0.190 (p. 180), and points to the probability that the second or  $\alpha$ -glucose radicle in maltose also undergoes conversion, either entirely or in part, into the  $\beta$ -modification when the sugar is dissolved in water, and that the constitution of dissolved maltose is:



The rotation, assuming that in a solution of maltose both glucose radicles are in the  $\beta$ -modification, may be calculated as follows:

Mag. rot. of 2 mols. $\beta$ -glucose .....	13.446
Less $H_2O$ .....	0.752
	<hr/>
	12.694
Found .....	12.690
	<hr/>
Diff. ....	0.004

The magnetic rotation of *lactose*, as already stated, was found to be 12.714, and if this value be examined, it will be seen it also indicates that lactose in solution contains both the galactose and glucose radicles in the  $\beta$ -condition. It has been seen that galactose when in solution is chiefly in the  $\alpha$ -condition; if, however, it were principally in the  $\beta$ -condition, its rotation, no doubt, would be similar to that of  $\beta$ -glucose, so that the rotation of lactose should be the same, or nearly so, as that of maltose, and this is found to be the case, the difference being only + 0.020. In the dry state, it probably has the formula proposed by E. Fischer, and this is, of course, equally true of maltose. Very probably these two carbohydrates, when in solution, always contain a little of the glucose radicle in the  $\alpha$ - or aldehydic condition.

#### EXPERIMENTAL.

##### *Erythritol*, $C_4H_{10}O_4$ .

This substance was purified by recrystallisation from water. The solution examined was supersaturated, containing 32.62 per cent. of erythritol, it being found possible to measure its rotation before crystallisation set in; the composition of the solution was  $C_4H_{10}O_4 + 14H_2O$ .

Density,  $d$  15°/15°, 1.1043;  $d$  20°/20°, 1.1033.

The average of three sets of determinations of the magnetic rotation made at different times was :

t.	Sp. rot.	Mol. rot. of sol.	Mol. rot. of $C_6H_{10}O_4$ .
15°.	1.0220	19.230	5.230

*Mannitol*,  $C_6H_{14}O_6$ .

This was recrystallised from water before use. As in the case of erythritol, a supersaturated solution was employed ; it contained 18.176 per cent. of mannitol, its composition being  $C_6H_{14}O_6 + 40H_2O$ .

. Density,  $d$  15°/15°, 1.0752 ;  $d$  20°/20°, 1.0746.

The average of four sets of measurements of the magnetic rotation made at different times gave :

t.	Sp. rot.	Mol. rot. of sol.	Mol. rot. of $C_6H_{14}O_6$ .
17.5°	1.0154	47.351	7.351

*Glucose*,  $C_6H_{12}O_6$ .

Two specimens of this substance were examined, one obtained from Kahlbaum, and the other, a very pure preparation, for which I am indebted to Dr. Horace Brown. With the former, four sets of measurements were made on different occasions and with solutions of various strengths, the most dilute being represented by  $C_6H_{12}O_6 + 20H_2O$ , and with that from Dr. Horace Brown also four measurements were made, but with only one strength, represented by  $C_6H_{12}O_6 + 11H_2O$  and containing 47.619 per cent. of  $C_6H_{12}O_6$ . The products used were the monohydrate dried over sulphuric acid in a vacuum :

The density of the solution  $C_6H_{12}O_6 + 11H_2O$  was  $d$  15°/15°, 1.2147 ;  $d$  20°/20°, 1.2135.

Magnetic rotation :

t.	Sp. rot.	Mol. rot. of sol.	Mol. rot. of $C_6H_{12}O_6$ .
15°	1.0261	17.723	6.723

The average of the measurements made with Kahlbaum's specimen was 6.715, which is very close to the above.

The permanent optical rotation of the solution containing 47.619 per cent. of  $C_6H_{12}O_6$  was  $[\alpha]_D$  56.22° at 16.9°. This is a little higher than that given for weak solutions.

If the magnetic rotations be calculated on the assumption that the glucose has assimilated a mol. of water and thus become a heptahydric alcohol, the solution will then have the composition  $C_6H_{14}O_7 + 10H_2O$ . The calculation will be the same as the above, only the value of 10 instead of 11 mols. of water will have to be subtracted from the mole-

cular rotation of the solution, and the rotation of the alcohol will thus become 7.723.

*Fructose*,  $C_6H_{12}O_6$ .

This was prepared from inulin and obtained from Kahlbaum. It was dried over sulphuric acid and its composition checked by a combustion; it gave C, 39.8, and H, 6.8, the formula  $C_6H_{12}O_6$  requiring C, 40.0, and H, 6.7 per cent. Its solution was examined in one strength only, containing 50 per cent. of fructose and represented by  $C_6H_{12}O_6 + 10H_2O$ .

Density,  $d_{15^\circ/15^\circ}$ , 1.2226;  $d_{20^\circ/20^\circ}$ , 1.2211.

The average of five sets of measurements of the magnetic rotation, made on different occasions, gave:

t.	Sp. rot.	Mol. rot. of sol.	Mol. rot. of $C_6H_{12}O_6$ .
15°	1.0227	16.729	6.729

Optical rotation  $[\alpha]_D$  96.19° at 15°.

*Galactose*,  $C_6H_{12}O_6$ .

This substance was examined in a very supersaturated solution, from which it does not crystallise very quickly. It contained 50 per cent. of the sugar, its composition being represented by  $C_6H_{12}O_6 + 10H_2O$ .

Density,  $d_{15^\circ/15^\circ}$ , 1.2311;  $d_{20^\circ/20^\circ}$ , 1.2299.

The average of four sets of measurements of the magnetic rotation, made on different occasions, gave

t.	Sp. rot.	Mol. rot. of sol.	Mol. rot. of $C_6H_{12}O_6$ .
15°	1.0396	16.887	6.887

Optical rotation  $[\alpha]_D$  84.23° at 14.6°.

*Sucrose*,  $C_{12}H_{22}O_{11}$ .

The specimen used was ordinary sugar recrystallised from alcohol (75 per cent.). The composition of the solution used was represented by  $C_{12}H_{22}O_{11} + 19H_2O$ , and contained 50 per cent. sucrose.

Density,  $d_{15^\circ/15^\circ}$ , 1.2327;  $d_{20^\circ/20^\circ}$ , 1.2316.

The magnetic rotation, determined on four different occasions, was:

t.	Sp. rot.	Mol. rot. of sol.	Mol. rot. of $C_{12}H_{22}O_{11}$ .
15°	1.0247	31.586	12.586

Optical rotation  $[\alpha]_D$  66.51° at 17°.



*Maltose*,  $C_{12}H_{22}O_{11}$ .

For a very pure specimen of this compound, I am indebted to Dr. Horace Brown. The solution employed contained 47.5 per cent. of the sugar, its composition being represented by  $C_{12}H_{22}O_{11} + 20H_2O$ .

Density,  $d_{15^\circ/15^\circ}$ , 1.2214 ;  $d_{20^\circ/20^\circ}$ , 1.2205.

The average of three sets of measurements of the magnetic rotation, made on different occasions, gave :

t.	Sp. rot.	Mol. rot. of sol.	Mol. rot. of $C_{12}H_{22}O_{11}$ .
15°	1.0288	33.690	12.690

Optical rotation  $[\alpha]_D$  137.0° at 16.7°.

*Lactose*,  $C_{12}H_{22}O_{11}$ .

This was obtained from Kahlbaum and was purified by fractional crystallisation, the crop deposited during the first 12 hours being rejected. It was dried in a vacuum over sulphuric acid. The solution used was a supersaturated one containing 33.333 per cent. of the sugar, and had the composition  $C_{12}H_{22}O_{11} + 41H_2O$ .

Density,  $d_{15^\circ/15^\circ}$ , 1.1413 ;  $d_{20^\circ/20^\circ}$ , 1.1406.

The magnetic rotation, as determined four times on different occasions, was :

t.	Sp. rot.	Mol. rot. of sol.	Mol. rot. of $C_{12}H_{22}O_{11}$ .
18.4°	1.0213	53.714	12.714

Optical rotation  $[\alpha]_D$  52.6° at 18°.

*Summary.*

The chief results obtained in this investigation go to show :

(1) That the influence of successive hydroxyl groups in polyhydric alcohols on the magnetic rotations diminishes as they increase in number, until about the seventh is reached, when it becomes almost *nil*.

(2) That solutions of glucose and fructose, after all change has taken place, give magnetic rotations which indicate that birotation is not due to hydration, but that it is caused by a change in the constitution of these substances.

(3) That galactose, when in solution, does not undergo isomeric change to so large an extent as glucose.

(4) That sucrose is built up of the isomeric or  $\beta$ -forms of glucose and fructose by the elimination of the elements of a mol. of water.

(5) That maltose is formed from 1 molecule of glucose in the aldehydic or  $\alpha$ -condition and 1 molecule in the isomeric or  $\beta$ -condition by the elimination of the elements of a mol. of water and that lactose is similarly derived from 1 molecule of  $\alpha$ -glucose and 1 of  $\beta$ -galactose, both being constituted in a similar manner to that proposed by E. Fischer for lactose, also that when in solution these sugars undergo isomeric change, the  $\alpha$ -portion becoming transformed, more or less, into the  $\beta$ -condition. This change accounts for the birotation and cupric reducing power of the two sugars.

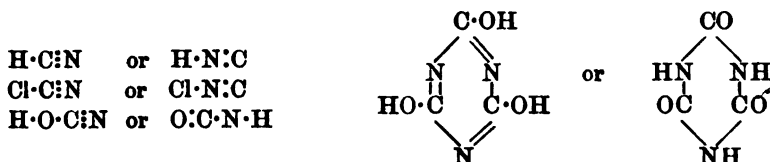
## XX.—*The Constitution of Hydrocyanic, Cyanic, and Cyanuric Acids.*

By F. D. CHATTAWAY and J. MELLO WADMORE.

ALTHOUGH the simplest cyanogen derivatives have been for more than a century among the most familiar of carbon compounds, there is no general agreement as to their constitution. They all contain a carbon and a nitrogen atom associated together, and different opinions are held as to the manner in which hydrogen or halogen atoms are attached to this group.

As a rule, well-defined classes of alkyl derivatives corresponding with each possible structure are known, the behaviour of which leaves no doubt concerning their molecular arrangement, but the reactions of the cyanogen acids, their salts and halogen derivatives, are contradictory, and apparently equally well-established facts lead to opposite conclusions.

Hydrocyanic acid, cyanogen chloride, cyanic and cyanuric acids, for example, may have the following structures:



The formulæ generally adopted are those given first, the hydrogen, halogen, and hydroxyl being regarded as attached to the carbon atom.

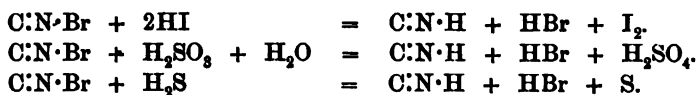
The knowledge which we have recently acquired of the strikingly different behaviour of halogen when attached to carbon or to nitrogen made it probable that a study of the action of halogens on the

cyanogen acids, and of the derivatives thereby produced, would afford direct evidence as to their constitution. Speaking generally, imino-hydrogen is more readily replaced by halogen than hydrogen attached to carbon, and the imino-halogen compounds are characteristically reactive, while the carbon halogen linkage is comparatively stable.

Cyanogen chloride, bromide, and iodide were among the earliest discovered compounds of cyanogen, as they are formed with the greatest ease by the action of the halogens on aqueous solutions of hydrocyanic acid or its salts. A careful study of the behaviour of these compounds shows that they possess all the typical and characteristic properties of compounds having halogen attached to nitrogen.

They react, for example, quantitatively with solutions of hydriodic acid, sulphurous acid, and hydrogen sulphide, hydrocyanic acid being in each case reformed, while iodine, sulphuric acid, and sulphur are respectively produced.

Taking cyanogen bromide, for example, the reactions are represented by the equations:



This behaviour shows that the halogen is attached to nitrogen and not to carbon in these compounds, and that, consequently, they must be represented by the formulæ:



The carbon is conventionally represented as divalent, and the nitrogen as trivalent; no very different conception, however, would be expressed if the carbon were represented as tetravalent and the nitrogen as pentavalent, since what is implied is that the carbon is attached to the nitrogen by the resultant affinity which, under the circumstances, the atoms are capable of exerting.

The ease with which the cyanogen halogen compounds can be formed from prussic acid and its salts, and again transformed into them, makes it in the highest degree probable that these have the imino-constitution, and hence should be represented by the formulæ:



This conclusion, moreover, is the only one which will satisfactorily explain their whole chemical behaviour.\*

The relations of the cyanides and cyanogen chloride to cyanic acid

\* We have not thought it necessary to go into explanatory details as these can be easily supplied.

and its salts have been among the chief reasons which led to the adoption of the hydroxy-formulæ :



for these compounds.

Since, as we have just shown, the former are imino-compounds these relations become reasons for adopting the alternative imino-structure :



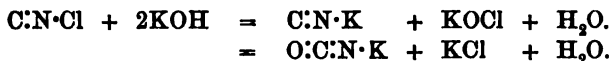
and



For example, the production of potassium cyanate, when cyanogen chloride is treated with aqueous potash, has been used as an argument for the hydroxy-constitution, since if the chlorine in cyanogen chloride is attached to carbon, it could be regarded as a normal case of hydrolysis :

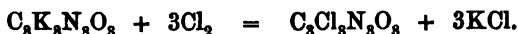


Cyanogen chloride, however, has the imino-structure, and the reaction becomes an argument in the other direction, for a comparison of this behaviour with that of the analogous cyanogen iodide shows that it must be regarded as a normal hydrolysis of a nitrogen chloride followed by oxidation of the potassium cyanide first formed :



Analogy with cyanuric acid also is in favour of the imino-structure.

The action of chlorine on a solution of potassium cyanurate is precisely similar to its action on potassium cyanide, the potassium atoms are replaced by chlorine, and a well-defined crystalline compound is produced, thus :

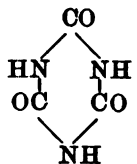


The entire chemical behaviour of this substance shows that the whole of its halogen is attached to nitrogen. It liberates chlorine when treated with hydrochloric acid, iodine with hydriodic acid, and oxidises sulphurous to sulphuric acid. Cyanuric acid is, in each case, reformed, and the reactions are quantitative ; the action with hydrochloric acid, for example, takes place according to the equation :

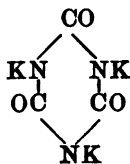


It is hydrolysed by water or alkalis, yielding hypochlorous acid or hypochlorites. It reacts explosively with a strong ammonia solution, nitrogen being liberated, and also with a solution of hydrogen sulphide, setting free sulphur. Cyanuric acid is in each case reformed. The compound must therefore be trichloriminocyanuric acid.

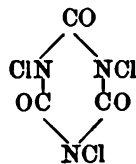
Since cyanurates are so readily and completely converted into this trichlorimino-derivative, and the latter in many reactions equally readily and completely again into cyanuric acid, we are justified in concluding that Hofmann was in error in assigning a hydroxy-constitution to the acid and its salts, and that, on the contrary, they have the imino-constitution, and assuming the correctness of the cyclic structure that they must be expressed by the formulæ



Cyanuric acid.



Potassium cyanurate.

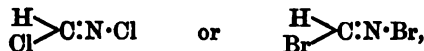


Trichlorimino-cyanuric acid.

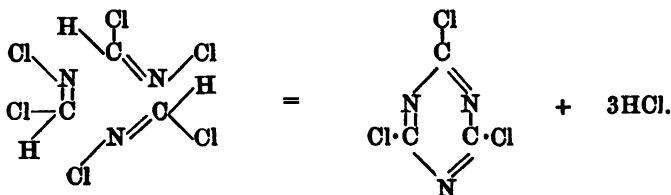
A similar study of the behaviour of cyanuric chloride and bromide confirms Hofmann's conclusion that in them the halogen is attached to the carbon and not to the nitrogen. They do not liberate iodine from hydriodic acid or sulphur from hydrogen sulphide, nor do they oxidise sulphurous acid, even when heated to 100° with these reagents.

This constitution, however, was to be expected from the structure of the cyanogen halogen compounds, from which they are produced by polymerisation under the influence of halogen acids.

Cyanogen chloride and bromide, as we have shown, are chlorimino-derivatives in which the carbon being unsaturated is able to combine with two monad atoms. In the polymerisation, the halogen acid in all probability first adds itself on forming molecules having the constitution :



which, on coming into contact, unite into ring systems of normal structure with elimination of halogen acid, thus :

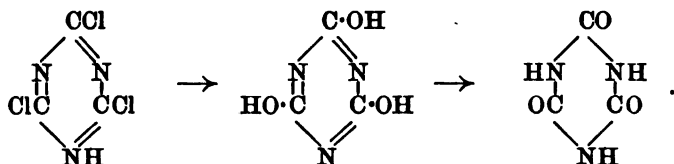


As Hofmann has pointed out, all the relations of the cyanogen group can only be explained by assuming isomeric change to occur in certain reactions ; the issue is as to where this takes place.

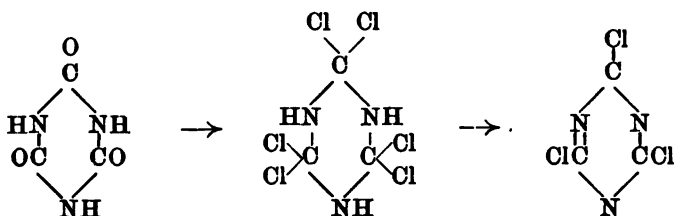
Cyanuric chloride, as is well known, yields cyanuric acid and hydrochloric acid on prolonged heating with water, the reaction being more rapid if alkalis are present. This and the corresponding conversion of cyanuric acid into cyanuric chloride by phosphorus pentachloride are the chief grounds on which Hofmann assigned the hydroxy-structure to the acid.

If, however, the views now put forward as to its constitution are correct, these are the reactions where isomeric change occurs, and analogous behaviour in other well-established cases renders this probable. We must assume that in the hydrolysis of cyanuric chloride normal cyanuric acid is first formed, but as in many cases where we have the grouping  $\begin{array}{c} \text{O}\cdot\text{H} \\ | \\ \text{--C=C--} \end{array}$ , the configuration is unstable

and passes into the stable arrangement  $\begin{array}{c} \text{O} \quad \text{H} \\ || \quad | \\ \text{--C--C--} \end{array}$ , so here we have an intramolecular change, the stable imino-form of ordinary cyanuric acid being the result :



The action of phosphorus pentachloride on cyanuric acid is probably analogous to its action on amides, the replacement of an oxygen atom by two chlorine atoms being followed by the elimination of hydrogen chloride :

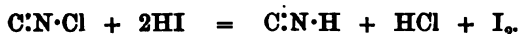


#### EXPERIMENTAL.

##### *Cyanogen Chloride, C<sub>2</sub>N<sub>2</sub>Cl.*

This compound shows the characteristic behaviour of a nitrogen chloride, although it reacts less readily than is usual with such substances. When hydriodic acid is added to an aqueous solution of cyanogen chloride at the ordinary temperature, very little iodine is liberated ; the amount, however, increases slowly on standing, rapidly

on heating to near 100°, until it reaches about 80 per cent. of that required by the equation:



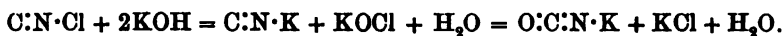
If the heating be prolonged, the free iodine slowly disappears, probably owing to hydrolysis of the hydrocyanic acid, and oxidation of the formic acid or ammonia produced.

When aqueous solutions of cyanogen chloride and hydrogen sulphide are heated together to 100°, sulphur is set free in considerable quantity; the hydrocyanic acid formed is mainly hydrolysed, but a small amount escapes decomposition and combines with some of the liberated sulphur to produce thiocyanic acid.

Similarly, when solutions of cyanogen chloride and sulphurous acid or sulphites are heated to 100°, the latter are oxidised while the hydrocyanic acid is destroyed, probably hydrolysed.

No liberation of chlorine can be detected when a solution of cyanogen chloride is heated with hydrochloric acid to 100°; the cyanogen chloride, however, is completely decomposed at this temperature.

The production of potassium cyanate and chloride by heating cyanogen chloride with caustic potash is probably due to the normal hydrolysis which all chlorimino-compounds undergo, followed by a subsequent oxidation of the cyanide by the hypochlorite formed.



#### *Cyanogen Bromide, C:N·Br.*

Cyanogen bromide is much more reactive than cyanogen chloride. At the ordinary temperature, it liberates iodine from hydriodic acid, sulphur from hydrogen sulphide, and oxidises sulphurous acid or sodium sulphite. All these reactions are quantitative, hydrocyanic and hydrobromic acids being formed in equivalent amount.

A weighed quantity of cyanogen bromide was added to an excess of a solution of hydriodic acid made by dissolving 10 grams of potassium iodide in 100 c.c. of a 5 per cent. solution of acetic acid; hydrocyanic acid and iodine were at once liberated, the latter being then estimated by sodium thiosulphate:

0.2439 liberated I = 46 c.c. *N*/10 iodine. Br as :N·Br = 75.4.\*

C:N·Br requires 75.43 per cent.

A weighed quantity of cyanogen bromide was added to an excess of an approximately decinormal solution of hydrogen sulphide; sulphur

\* Throughout this paper the results are calculated on the assumption that the substances under consideration react as typical nitrogen halogen compounds, the numbers are then compared with the percentages calculated from the formulæ.

was at once deposited and hydrobromic and hydrocyanic acids formed, together with a little thiocyanic acid, produced by the action of the sulphur on the latter; the excess of hydrogen sulphide was then estimated by a solution of iodine:

0.4791 reacted with 90.7 c.c.  $N/10$   $H_2S/2$ . Br as  $:N \cdot Br = 75.68$ .

$C:N \cdot Br$  requires 75.43 per cent.

A similar procedure was adopted in studying the reaction with sulphurous acid. A weighed quantity of cyanogen bromide dissolved in dilute acetic acid was added to an excess of a decinormal solution of sodium sulphite, and then the excess of the latter estimated by a solution of iodine:

0.5050 reacted with 95.25 c.c.  $N/10$   $Na_2SO_3/2$ . Br as  $:N \cdot Br = 75.41$ .

$C:N \cdot Br$  requires 75.43 per cent.

No bromine is liberated when cyanogen bromide is heated with a solution of potassium bromide made acid with acetic acid, or when it is heated with strong hydrochloric acid to  $100^\circ$ , although in the latter case it is decomposed just as cyanogen chloride is when similarly treated.

### *Cyanogen Iodide.*

Cyanogen iodide is more reactive than cyanogen chloride or cyanogen bromide, and behaves as a typical nitrogen iodide. It reacts with hydriodic acid, liberating iodine, with hydrobromic acid liberating bromine and iodine, with hydrochloric acid forming iodine monochloride; it oxidises sulphurous acid and sodium sulphite, forming sulphates and sets free sulphur from hydrogen sulphide. Its behaviour towards several of these substances was very carefully studied by E. von Meyer (*J. pr. Chem.*, 1887, [ii], 35, 292). He showed that the reaction between hydrocyanic acid and iodine is a reversible one, and that two molecules of sulphur dioxide completely reduce two molecules of cyanogen iodide to hydrocyanic and hydriodic acids. He, however, writes the formula  $ICN$ , and concludes his paper by stating that it is the only oxygen-free iodide soluble in water which shows the surprising behaviour of liberating iodine under the action of reducing agents, but of remaining unattacked by reagents which set iodine free from other iodides.

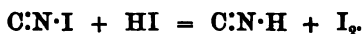
We have quantitatively studied the behaviour of cyanogen iodide in order to compare it with that of the bromide and the chloride. A weighed quantity of cyanogen iodide was added to an excess of a solution of 10 grams of potassium iodide in 5 per cent. acetic acid; hydrocyanic acid and iodine were at once liberated, the amount of the latter being then estimated by sodium thiosulphate:

0.2964 liberated  $I = 38.8$  c.c.  $N/10$  iodine.  $I$  as  $:N \cdot I = 83.02$ .

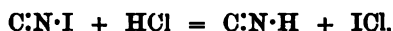
$C:N \cdot I$  requires 82.97 per cent.



This result is exactly that required by the equation :



When cyanogen iodide is dissolved in an excess of strong hydrochloric acid at the ordinary temperature, very little action takes place, but on warming to 20—30° the liquid becomes orange-coloured, owing to the formation of iodine monochloride, and the colour deepens as the temperature rises. There is no liberation of free iodine even on boiling the solution. Hydrocyanic acid is also produced. In one experiment, the iodine monochloride was distilled off into a solution of potassium iodide, and the liberated iodine estimated. The amount of iodine monochloride obtained was about 2 per cent. below that required by the equation



The loss is probably due to the hydrolysis of a small amount of the hydrocyanic acid and partial oxidation by the iodine monochloride of the products.

When cyanogen iodide is similarly treated with hydrobromic acid, both iodine and bromine are evolved, but, as with hydrochloric acid, the amount falls somewhat short of that required by the equation



probably from a similar cause.

When a solution of sulphurous acid is slowly added to cyanogen iodide, iodine is liberated, hydrocyanic acid and sulphuric acid being simultaneously formed ; if, however, the iodide be added to an excess of sulphurous acid, no liberation of halogen occurs (compare Strecker, *Annalen*, 1868, 148, 90).

A weighed quantity of cyanogen iodide was added to an excess of a decinormal solution of sodium sulphite so that no iodine was set free, and the excess of sulphite estimated by a dilute solution of iodine :

0.2960 oxidised 38.7 c.c. of  $N/10 \text{ Na}_2\text{SO}_3/2$ . I as :N:I = 82.92.

C:N:I requires 82.97 per cent.

The action takes place according to the equation



Sulphur is set free and hydrocyanic and hydriodic acids are formed when cyanogen iodide is added to an excess of a solution of hydrogen sulphide. If the latter is slowly added to the iodide, iodine is also liberated, owing to the action of the hydriodic acid first formed on the unchanged cyanogen iodide. A little thiocyanic acid also is always formed from the interaction of some of the hydrocyanic acid with the sulphur.

In the following experiment, cyanogen iodide was added to an excess of hydrogen sulphide, the amount of the latter remaining unacted on being estimated by a solution of iodine :

0.2896 reacted with 37.9 c.c.  $N/10$   $H_2S/2$ . I as  $\cdot N \cdot I = 83$ .

$C:N \cdot I$  requires 82.97 per cent.

The result is expressed by the equation



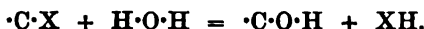
Its behaviour towards a solution of potassium hydrate also shows that in it the halogen is attached to nitrogen, and affords an explanation of the apparently different action of the similarly constituted cyanogen chloride and bromide.

When it is added to a boiling solution of caustic potash, it is at once decomposed ; among other products, a small quantity of potassium iodate is formed. Cyanogen chloride and bromide, when similarly treated, form no chlorate or bromate. All the cyanogen halogen compounds, however, are readily decomposed by caustic alkalis, yielding cyanates.

The nitrogen halogen linkage, as is well known, behaves in a characteristic way on hydrolysis, the halogen being invariably replaced by hydrogen and becoming itself attached to the residual hydroxyl, thus :



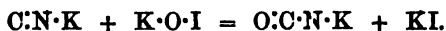
It is thus sharply distinguished from the carbon halogen linkage, where the opposite happens, thus :



The formation of iodate in the reaction between cyanogen iodide and potash shows that, at first, nitrogen halogen hydrolysis undoubtedly takes place, thus :



A certain amount of the hypiodite, on account of the ease with which it is transformed into iodide and iodate, escapes reduction by the cyanide simultaneously formed, a reaction which results in the production of cyanate :

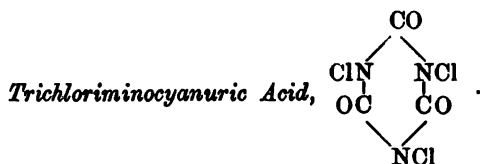
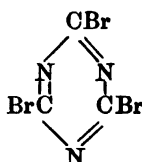
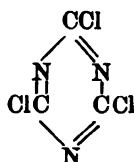


In the cases of cyanogen chloride and bromide, the hypochlorite and hypobromite, which must first be formed, do not transform so readily, and consequently are wholly reduced.

*Cyanuric Chloride and Bromide.*

These compounds show none of the reactions characteristic of the halogen nitrogen linkage.

Small quantities of each were taken and heated for 30 minutes at 100° in stoppered bottles, air being excluded, with solutions of hydriodic acid, hydrogen sulphide, and sodium sulphite. No iodine or sulphur was liberated, nor was the sulphite oxidised. This behaviour is in agreement with Hofmann's view of their constitution, deduced from altogether different reactions, and with the formula assigned to them by him and generally adopted:



This compound is prepared with the greatest ease by dissolving cyanuric acid in the theoretical quantity of a 5 per cent. solution of caustic potash and passing a rapid stream of chlorine through the liquid cooled to 0°.

Trichloriminocyanuric acid separates as a heavy, white, crystalline powder which is obtained perfectly pure by washing a few times with water and drying rapidly on a water-bath:



Using about 3 grams of acid, a yield of more than 90 per cent. of the theoretical is obtained. If a larger quantity than this be used or the temperature be allowed to rise, the yield is much diminished and the product is more or less impure.

Trichloriminocyanuric acid is a white, crystalline powder which, under the microscope, is seen to consist of short prisms. It has a characteristic odour resembling that of hypochlorous acid. It dissolves to some extent in water and glacial acetic acid on heating, but the greater part undergoes hydrolysis; it is very slightly soluble in chloroform, but insoluble in light petroleum. It melts at about

245°. Its behaviour is in every way that of a typical nitrogen chloride. When added to strong hydrochloric acid, chlorine is liberated, the halogen escaping rapidly with effervescence; it liberates bromine from hydrobromic acid, iodine from hydriodic acid; it oxidises sulphites to sulphates and sets free sulphur from hydrogen sulphide, cyanuric acid in all cases being reformed. When added to ammonia a violent action which may become explosive takes place, nitrogen is evolved, and cyanuric acid reformed. When boiled with water, dilute acids or alkaline hydroxides, it is hydrolysed, cyanuric acid and hypochlorites or the products of their transformation chlorides and chlorates, being produced.

The percentage of chlorine was estimated by Carius' method, and several of the reactions referred to above have been quantitatively studied:

0.3280 gave 0.6052 AgCl. Cl = 45.62.

$\text{O}_3\text{C}_3\text{N}_3\text{Cl}_3$  requires Cl = 45.75 per cent.

A weighed quantity was added to a solution of potassium iodide, made acid with acetic acid, and the iodine liberated estimated by thiosulphate:

0.4177 liberated I = 107.9 c.c. *N*/10 iodine. Cl as :N·Cl = 45.78.

$\left( \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{Cl} \end{array} \right)_3$  requires 45.75 per cent.

A weighed quantity was dissolved in acetic acid, an excess of an approximately decinormal solution of sodium sulphite was added, and the excess afterwards estimated by a standard solution of iodine.

0.2783 oxidised 71.9 c.c. *N*/10  $\text{Na}_2\text{SO}_3/2$ . Cl as :N·Cl = 45.79.

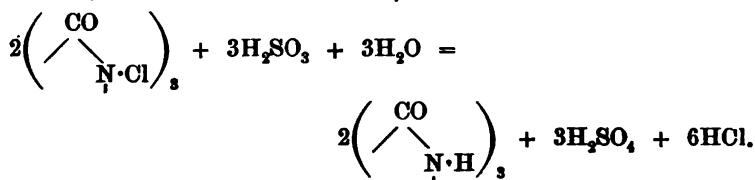
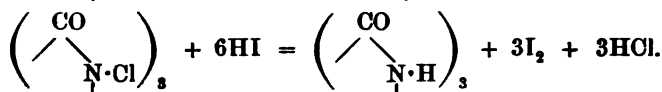
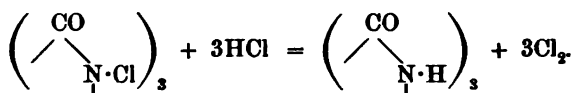
$\left( \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{Cl} \end{array} \right)_3$  requires 45.75 per cent.

A weighed quantity was heated with an excess of strong hydrochloric acid, in a current of carbon dioxide, in an apparatus with ground glass joints (*Chem. News*, 1899, 85) and the evolved chlorine passed into a solution of potassium iodide.

0.4689 evolved Cl = 120.9 c.c. *N*/10 iodine. Cl as :N·Cl = 45.7.

$\left( \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{Cl} \end{array} \right)_3$  requires 45.75 per cent.

These actions are represented by the equations:



The reaction with hydrogen sulphide cannot be used to estimate the amount of chlorine attached to nitrogen, as this substance, like all nitrogen chlorides, oxidises a variable amount of the liberated sulphur to sulphuric acid.

#### *Action of Bromine on Potassium Cyanurate.*

When bromine is added to a solution of cyanuric acid in the theoretical amount of a 5 per cent. solution of caustic potash, a pale yellow substance separates from the liquid. This on exposure to air rapidly decomposes, bromine being evolved; it cannot therefore be freed from water and analysed. It liberates iodine from hydriodic acid and violently decomposes ammonia with evolution of nitrogen, cyanuric acid being reformed in each case. When dried over sulphuric acid in an atmosphere of bromine, a pale orange-coloured powder is obtained which gives off bromine slowly at the ordinary temperature, rapidly at 100°, leaving an orange powder having properties similar to those of the original substance. We have not yet been able to obtain a product which we could regard as a pure substance, the composition varying considerably with slight differences of procedure. A very large number of analyses of different specimens seems to show that the body first formed is a bromine additive product of a bromimino-derivative of cyanuric acid, in which, however, all the imino-hydrogen of the cyanuric acid is not replaced.

#### *Action of Chlorine and Bromine on Potassium Cyanate.*

Attempts to prepare a chlorimino-derivative of cyanic acid have hitherto been unsuccessful. When chlorine is passed into a cold solution of potassium cyanate, it is absorbed, gas is evolved, and a white, crystalline powder separates, a very pungent odour, somewhat resembling that of cyanogen chloride, being noticed during the reaction.

The white solid thus obtained is, however, cyanuric acid containing a little (5 to 6 per cent.) trichloriminocyanuric acid; on treating with hydrochloric acid or ammonia to decompose the latter and recrystallising from water, pure cyanuric acid is obtained.

The action of bromine on a solution of potassium cyanate is similar and results in the production either of cyanuric acid or of the product already described as resulting from the action of bromine on a solution of potassium cyanurate. If bromine be added to a 25 per cent. solution of potassium cyanate, rapid evolution of nitrogen and carbon dioxide (approximately in the proportion  $N_2 : 2CO_2$ ) takes place, and the temperature rises to about  $80^\circ$ , if the addition be continued until an excess has been added and this be then removed by boiling; cyanuric acid crystallises out on cooling. If the solution of cyanate be cooled in a freezing mixture and the bromine be added cautiously, similar effervescence takes place and a yellow solid separates which in its composition and reactions resembles closely that obtained by the action of bromine on potassium cyanurate; for example, it liberates iodine from hydriodic acid and nitrogen from ammonia, cyanuric acid being in each case produced.

We are at present engaged in a study of various other reactions of the cyanogen halogen derivatives which appears likely to throw additional light on their structure.

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## XXI.—*Myricetin. Part II.*

By ARTHUR GEORGE PERKIN, F.R.S.E.

MYRICETIN was first isolated from the bark of the *Myrica nagi* (Trans., 1896, 69, 1287), and subsequently was found to be present in the leaves of *Rhus coriaria*, *cotinus*, and *metopium*, in the *Myrica gale*, *Pistachia lentiscus*, and *Hæmatoxylon campeachianum*. Its molecular weight is represented by the formula  $C_{15}H_{10}O_8$ ; it forms crystalline acid compounds, an hexa-acetyl derivative, and by fusion with alkali yields phloroglucinol and gallic acid; these facts, together with the similarity of its dyeing properties and those of quercetin, indicate that it has the constitution of an hydroxyquercetin. The quantity of colouring matter available for the above experiments was very small, as the *Myrica nagi* contained but 0.27 per cent., and sumach only 0.11 per cent.; moreover, the stock of the former, a material not easy to obtain, was soon exhausted. Although attempts to accumulate

sufficient myricetin were made from time to time, they had to be abandoned, and it is only lately, owing to the kindness of Professor E. Joshitake, of Tokio, that an extract of the *Myrica nagi* was obtained, by means of which the following work could be carried out.

#### EXPERIMENTAL.

The extract, a brownish-black, brittle mass, was treated with ten times its weight of hot water, and when cold the clear liquid was decanted, the residue again washed twice in a similar manner, and drained on a porous tile. It was digested with boiling alcohol, filtered from insoluble matter, and the filtrate evaporated until crystals separated; these were collected by means of the pump,\* washed, first with a little alcohol and then repeatedly with increasingly dilute alcohol until the washings were almost colourless. The yellowish-brown residue was crystallised from dilute alcohol, then converted into its acetyl compound, and the latter, when pure, decomposed with acid in the usual manner. It was incidentally determined that the melting point, 204—206°, previously given for acetylmuricetin, is somewhat too low, and should be 211—212°. An analysis of myricetin was again made:

0.1332 gave 0.2744 CO<sub>2</sub> and 0.0389 H<sub>2</sub>O. C = 56.18; H = 3.24.

C<sub>15</sub>H<sub>10</sub>O<sub>8</sub> requires C = 56.60; H = 3.14 per cent.

When crystallised from dilute alcohol, and allowed to dry, myricetin has the formula C<sub>15</sub>H<sub>10</sub>O<sub>8</sub>.H<sub>2</sub>O, and this water of crystallisation is best removed by heating at 160°, although it is almost entirely evolved at 100°:

0.5367 at 160° lost 0.0290 H<sub>2</sub>O. Found 5.40.

0.4686 „ 160° „ 0.0249 H<sub>2</sub>O. „ 5.31.

Theory requires H<sub>2</sub>O = 5.35 per cent.

Myricetin melts between 355° and 360°. Owing, however, to the darkening of the tube, it was difficult to be certain to one degree, although 357° is probably correct.

**Bromine Compound.**—By the action of bromine on myricetin suspended in glacial acetic acid, a compound was previously obtained which had the percentage composition of tetrabromomyricetin (*loc. cit.*). Owing to its soluble nature and peculiar dyeing properties, some doubt as to its constitution was expressed, it being possible that during the reaction a decomposition had ensued. To determine this point, the bromine compound was digested for several hours with boiling hydriodic acid and the product treated with sodium bisul-

\* Filtrate A (see p. 207).

phite solution. The resulting yellow precipitate crystallised from dilute alcohol in needles which had all the properties of myricetin and gave a colourless acetyl derivative melting at 211—212°. The compound in question was thus without doubt *tetrabromomyricetin*.

### *Methylation of Myricetin.*

Four grams of myricetin, dissolved in boiling methyl alcohol containing excess of methyl iodide, were treated drop by drop with a solution of eight grams of caustic potash in methyl alcohol, the addition extending over a day and a half. This procedure was adopted with the object of preventing an oxidation of the myricetin, which readily occurs in the presence of alkali. After removal of unattacked methyl iodide and the greater portion of the alcohol by distillation, the residue was treated with water, extracted with ether, and the ethereal solution washed with dilute caustic potash solution. On evaporation, a semicrystalline product remained which was purified by repeated crystallisation from alcohol:

0.1163 gave 0.2630  $\text{CO}_2$  and 0.0574  $\text{H}_2\text{O}$ . C = 61.67; H = 5.48.

0.1134 „ 0.2553  $\text{CO}_2$  „ 0.0549  $\text{H}_2\text{O}$ . C = 61.40; H = 5.37.

0.1000 „ 0.3040 AgI.  $\text{CH}_3$  = 19.40.

$\text{C}_{15}\text{H}_8\text{O}_8(\text{CH}_3)_5$  requires C = 61.85; H = 5.15;  $\text{CH}_3$  = 19.33 per cent.

*Myricetin pentamethyl ether* forms very pale yellow, almost colourless, hair-like needles melting at 138—139°, and is sparingly soluble in cold alcohol. On acetylation in the usual manner, it gives an acetyl derivative which crystallises from alcohol in colourless needles melting at 167—170°. Decomposition with acid indicated the presence of one acetyl group:

0.4342 gave 0.3895 regenerated ether. Found 89.70.

Theory for loss of one acetyl group requires 90.23 per cent.

Myricetin thus contains one hydroxyl group which resists methylation, and is consequently in the ortho-position to a carbonyl group. On treatment with alcoholic potash, the pentamethyl ether yields a yellow potassium salt readily decomposed by water.

On digestion with alcoholic potash at 170° for three hours, myricetin pentamethyl ether was decomposed, and from the product of the reaction an acid and a phenol were isolated. The acid crystallised in colourless needles melting at 164—167°, and was found to be *gallic acid trimethyl ether*.

The viscous, readily soluble phenol yielded an azobenzene derivative which crystallised from a mixture of alcohol and acetic acid in orange-red leaflets melting at 250—252°. This compound is identical with that given by rhamnetin, quercetin tetramethyl ether (Proc.,



1900, 181), and luteolin trimethyl ether under similar conditions and is consequently *disazobenzene phloroglucinol monomethyl ether*. The phenol is thus *phloroglucinol monomethyl ether*.

### *Ethylation of Myricetin.*

Five grams of myricetin dissolved in a boiling mixture of alcohol and ethyl iodide were treated during 12 hours with a solution of 9.5 grams of caustic potash in alcohol, drop by drop. The product of the reaction insoluble in alkali was purified by crystallisation from alcohol:

0.1064 gave 0.2600  $\text{CO}_2$  and 0.0682  $\text{H}_2\text{O}$ . C = 66.64; H = 7.12.

0.1124 „ 0.2730  $\text{CO}_2$  „ 0.0710  $\text{H}_2\text{O}$ . C = 66.24; H = 7.01.

$\text{C}_{15}\text{H}_4\text{O}_8(\text{C}_2\text{H}_5)_6$  requires C = 66.66; H = 6.99 per cent.

It forms almost colourless needles melting at 149—151°, sparingly soluble in cold alcohol. This compound does not contain a free hydroxyl group, for after digestion with acetic anhydride and sodium acetate, its melting point and percentage composition (found C = 66.56; H = 7.01) were unaltered. Further, this product, on treatment with sulphuric acid, sustained no loss, 0.4112 and 0.8174 yielding respectively 0.4116 and 0.8173 gram of unchanged substance. It is thus without doubt *myricetin hexaethyl ether*.

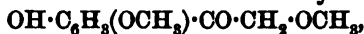
When decomposed with alcoholic potash at 170°, it yielded, like the methyl ether, an acid and a phenol. The former crystallised from water in colourless needles or leaflets melting at 111—112°. It was found to be *gallic acid triethyl ether*:

0.1093 gave 0.2460  $\text{CO}_2$  and 0.0717  $\text{H}_2\text{O}$ . C = 61.38; H = 7.28.

Theory requires C = 61.41; H = 7.09 per cent.

The phenol dissolved in dilute sodium carbonate solution gave, with diazobenzene sulphate, a bright yellow precipitate, which was collected, washed, dried, and purified by several crystallisations from benzene. It formed glistening, bright yellow needles melting at 163—165°, but on account of its ready solubility in the usual solvents, sufficient was not available for analysis. From analogy, however, it is probably *azobenzene phloroglucinol diethyl ether*.

When fisetin tetramethyl ether is decomposed with boiling alcoholic potash, it yields veratric acid and fisetol dimethyl ether,



a fact which enabled Herzig (*Monatsh.*, 1891, 12, 187) to determine the constitution of fisetin. At this lower temperature, myricetin hexaethyl ether is also decomposed, but the products were identical with those given by alcoholic potash at 170°, and it thus appears likely that the anticipated phloroglucinol derivative is too unstable to be produced by

this method. The matter is worthy of further experiment, but owing to lack of raw material this at present is impossible.

*Monopotassium Myricetin*.—When a boiling solution of myricetin in absolute alcohol is treated with alcoholic potassium acetate, an orange-red, amorphous precipitate separates; if, however, a slightly dilute alcohol be employed, the substance is obtained in a crystalline condition. It was collected and washed with alcohol, and dried at  $100^{\circ}$ , when it assumed a dark green colour. When digested with boiling water, it is decomposed, with separation of myricetin:

Found  $K = 11.95$ .  $C_{15}H_9O_6K$  requires  $K = 10.95$  per cent.

Owing possibly to oxidation, the salt could not be obtained in a chemically pure condition, but the result is sufficient to prove that myricetin reacts in an analogous manner to quercetin and the other colouring matters of this group.

#### *A Glucoside of Myricetin.*

The alcoholic filtrate (A, p. 204) from the crude myricetin, on standing overnight, became semisolid owing to the deposition of crystals. These were drained from the black, tarry mother liquor, washed first with a little alcohol and then with 50 per cent. alcohol until the filtrate was nearly colourless. The product was dissolved in boiling water, filtered from a small quantity of myricetin, and the crystals which separated on cooling again treated in a similar manner. It was now twice crystallised from alcohol, and again from water. *Myricitrin*, the name proposed for this glucoside, crystallises from water in pale yellow, almost colourless leaflets containing one molecule of water of crystallisation; this cannot be removed at  $100^{\circ}$ , but is completely evolved at  $160^{\circ}$ :

1.0925 at  $160^{\circ}$  gave 0.0420  $H_2O$ . Found 3.84.

1.1390 „  $160^{\circ}$  „ 0.0475  $H_2O$ . Found 4.17.

Theory requires  $H_2O = 3.60$  per cent.

0.1185 at  $100^{\circ}$  gave 0.2205  $CO_2$  and 0.0520  $H_2O$ .  $C = 50.74$ ;  $H = 4.87$ .

0.1098 „  $160^{\circ}$  „ 0.2098  $CO_2$  „ 0.0445  $H_2O$ .  $C = 52.10$ ;  $H = 4.50$ .

0.1150 „  $160^{\circ}$  „ 0.2181  $CO_2$  „ 0.0475  $H_2O$ .  $C = 51.72$ ;  $H = 4.59$ .

$C_{21}H_{22}O_{13} \cdot H_2O$  requires  $C = 50.40$ ;  $H = 4.80$  per cent.

$C_{21}H_{22}O_{13}$  „  $C = 52.28$ ;  $H = 4.56$  „

When slowly heated, it sinters at  $197^{\circ}$  and melts at  $199$ — $200^{\circ}$ , and is sparingly soluble in water and absolute alcohol. It dissolves in dilute alkaline solutions with a pale yellow colour having a faint green tint and this solution rapidly becomes brown on exposure to air. Aqueous lead acetate gives a gelatinous, orange-yellow precipitate, and alcoholic ferric chloride a deep, greenish-black coloration. In appearance, it

cannot be distinguished from quercitrin, and the dyeing properties of the two substances are almost identical :

	Chromium.	Aluminium.	Tin.	Iron.
Quercitrin.	Full brown-yellow.	Full golden-yellow.	Lemon-yellow.	Deep olive.
Myricitrin.	Full brown-yellow.	Full golden-yellow.	Lemon-yellow.	Brown-olive

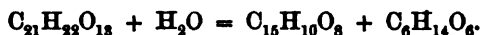
*Decomposition of the Glucoside.*—One gram (approx.) of myricitrin, dissolved in 500 c.c. of water, was treated with 1 c.c. of sulphuric acid and digested at the boiling temperature for 45 minutes. Crystals of myricetin separated out, and, after standing overnight, were collected washed, and dried at 160° :

1.0835	air-dried glucoside gave	0.6915	$C_{15}H_{10}O_8$ .	Found 63.85.
1.1660	dried at 100°	„	0.7427 $C_{15}H_{10}O_8$ .	Found 63.69.
1.0380	„ „ 160°	„	0.6800 $C_{15}H_{10}O_8$ .	Found 65.51.
$C_{21}H_{22}O_{13} \cdot H_2O$ requires $C_{15}H_{10}O_8 = 63.60$ per cent.				
$C_{21}H_{22}O_{13}$ „ $C_{15}H_{10}O_8 = 65.97$ „				

The free colouring matter had all the reactions of myricetin.

*The Sugar.*—The acid filtrate from the myricetin was neutralised with barium carbonate, filtered, and evaporated to a small bulk. The residue yielded a crystalline osazone, which was collected, washed with a little ether, recrystallised from alcohol, and finally from alcohol and water. It formed yellow needles melting at 181—183°, and was identical in properties with *rhamnose osazone*, a sample of which was prepared for comparison from the pure sugar.

Myricitrin, on hydrolysis, thus gives myricetin and rhamnose, and this reaction may be expressed as follows :

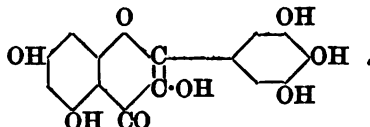


It is analogous to quercitrin which, in a similar manner, yields rhamnose and quercetin.



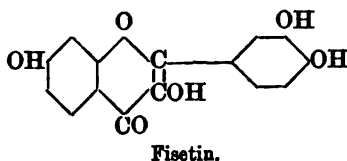
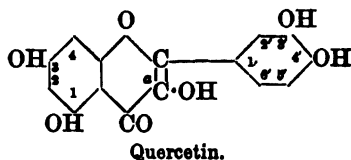
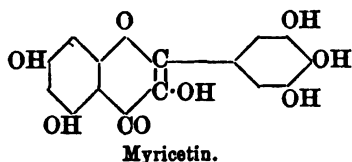
#### THEORETICAL.

The remarkable similarity between the reactions of quercetin and myricetin, previously pointed out (*loc. cit.*), is enhanced by the above results, and there seems no reason to doubt that myricetin is *hydroxy-quercetin*.

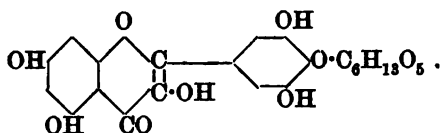


It is interesting that myricetin can so readily be fully ethylated with formation of a hexaethyl ether, whereas quercetin, although con-

taining five hydroxyl groups, gives but a tetraethyl derivative. This distinction is not of importance, in view of the behaviour in this respect of other members of the flavone group. Apigenin (Trans., 1897, 72, 805),  $C_{15}H_7O_2(OH)_3$ , has given a dimethyl and a diethyl ether; luteolin (Trans., 1900, 77, 1314),  $C_{15}H_6O_2(OH)_4$ , a dimethyl ether of methyl-luteolin and tetraethyl-luteolin (Herzig, *Ber.*, 1897, 30, 656), and campherol,  $C_{15}H_7O_2(OH)_3$ , a dimethyl ether of methyl-campherol (Testoni, *Gazzetta*, 1900, 30, ii, 327); such results are thus evidently due to the presence or absence of certain hydroxyl groups in these compounds, although in what manner they effect the reaction is not at present clear. The resemblance between the dyeing properties of quercetin and myricetin has been already alluded to, but it is most interesting that quercitrin and myricitrin should behave almost identically in this respect. These results indicate as probable that in both compounds the sugar group is present in the same position; further, it is possible, from a knowledge of the dyeing properties of some members of the flavone series, to indicate with some certainty the locality of this in myricitrin at least. The shades produced from fisetin, quercetin (Trans., 1896, 69, 1287) and myricetin



are similar in strength and character, and the resemblance in this respect between quercetin and rhamnetin (quercetin monomethyl ether,  $OOCH_3=3$ ) has also been pointed out. Consequently, it is evident that the hydroxyls 3 and 1 do not appreciably influence the colouring effect of quercetin or myricetin, the character of which is due to the orthohydroxyls they contain in conjunction with that present in the pyrone ring. Now, the dyeing properties of quercitrin and myricitrin are almost identical with those of morin, the constitution assigned to which (Trans., 1896, 68, 792) is very similar to that of myricetin, from which the hydroxyl (4') has been removed. It is thus likely that myricitrin has the constitution



and that that of quercitrin may be similarly expressed. The only alternative formula for myricitrin is that in which the sugar group has the position (a); such a compound should, by analogy, dye like luteolin, the shades of which (*loc. cit.*) do not widely differ from those given by morin. Employing the monopotassium derivatives of quercetin and myricetin (*loc. cit.*), experiments will be carried out with the hope of preparing glucosides of these colouring matters.

The expense incurred during this work has been largely defrayed by a grant from the Research Fund of the Chemical Society, and for this the author desires to acknowledge his indebtedness.

CLOTHWORKERS' RESEARCH LABORATORY,  
DYEING DEPARTMENT,  
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## XXII.—*The Colouring Matters of Green Ebony.*

By ARTHUR GEORGE PERKIN, F.R.S.E., and SAMUEL HENRY CLIFFORD BRIGGS, B.Sc.

GREEN ebony is a yellow dyewood formerly employed to some extent in this country, but now almost entirely replaced by other colouring matters. It is native of Jamaica or West India, and according to the "Treasury of Botany" (1884, p. 437) is obtained from *Excoecaria glandulosa* or *Jacaranda ovalifolia*, but the botanical name of that employed here is not certain, as this information could not be derived from a specimen of the wood alone. The trunk of the tree is about six inches in diameter, and the wood, which is very hard and of an orange-brown colour, stains the hands yellow when freshly cut. References to this dyestuff are meagre, and it does not appear to have been largely employed. Bancroft ("Philosophy of Permanent Colours," II, 106, 1813) states, "The wood known in England by the name of green ebony, possesses a species of colouring matter very similar to that of *Morus tinctoria* in dyeing, and is sometimes employed in its stead," and C. O'Neill ("Dictionary of Calico Printing and Dyeing," 1862) men-

tions that it is "used principally in dyeing greens and other compound shades." Until recently, it had a limited sale in Yorkshire as a dye for leather, particularly hat linings, but appears to have entirely passed out of use as a woollen dyestuff. According to Sir Thomas Wardle, it is little used in silk dyeing now, but was formerly employed for greening blacks, or making the shade more jet coloured. It was a good deal used for making shades less bright or flatter in tone, and in France in the "avivage" to give a slightly yellowish tint if the shade required it. The raw material was obtained by purchase from Messrs. James Richardson and Sons, of Leeds.

#### EXPERIMENTAL.

The rasped wood was extracted for six hours with ten times its weight of boiling water, and the decoction strained through calico. When cold, the orange-brown solution was saturated with salt, and the resulting somewhat viscous precipitate (C) collected, drained upon a porous tile, and allowed to dry. This product was extracted with boiling alcohol for four hours, the extract evaporated to a small bulk, and poured into a large volume of ether, which caused the separation of a dark-coloured, tarry mass devoid of tinctorial property; this was removed by decantation and the ethereal liquid repeatedly washed with water and evaporated to dryness. The viscous residue was dissolved in boiling alcohol, alcoholic lead acetate added, and the resulting orange-red precipitate repeatedly washed with boiling alcohol and finally with boiling water. It was now suspended in cold water, decomposed with a few drops of sulphuric acid, and the mixture of lead sulphate and colouring matter collected, washed, allowed to dry, and extracted with boiling alcohol. After evaporation to a small bulk, the solution was poured into ether, the mixture washed with water until a tarry impurity no longer separated, and after removal of the ether, the residue was dissolved in boiling absolute alcohol. On standing overnight, crystals of the colouring matter A, separated, which were collected and washed with alcohol. From the orange-brown, viscous filtrate, containing chiefly the resin A, on spontaneous evaporation and resolution in a little cold alcohol, a further quantity of the crystals was isolated. Different samples of the wood varied considerably, 8000 grams of a good material yielding 3.15 grams of crude colouring matter, A, whereas others gave as little as 1 gram, or even less.

The alcoholic filtrate from the lead precipitate was evaporated to a small bulk, poured into ether, and the mixture washed with water until tarry matter no longer separated. After removing most of the ether, chloroform was added, and the crystals of the colouring matter

B which separated were collected and washed with chloroform. The filtrate, on evaporation, yielded the resinous substance B. Eight thousand grams of the wood usually gave about 17 grams of this second colouring matter, but this again varied according to the material employed. From the aqueous filtrate from the precipitate C, by extraction with ether, approximately 0.3 gram could be isolated for each kilo. of the wood employed, but this was eventually run to waste on account of the costly nature of the operation.

As the yield of these crystalline substances was so small, it was found more economical to collect a considerable quantity of the precipitate C and work this up in one operation.

### *The Colouring Matter B.*

The crude material was dissolved in boiling alcohol, the solution evaporated to half its bulk, and, while hot, treated with an equal volume of boiling chloroform. The crystals which separated were collected on the pump, washed two or three times with a little cold ether, and recrystallised in a similar manner:

0.1178 gave 0.2714  $\text{CO}_2$  and 0.0532  $\text{H}_2\text{O}$ . C = 62.83; H = 5.01.

0.1180 „ 0.2720  $\text{CO}_2$  „ 0.0480  $\text{H}_2\text{O}$ . C = 62.86; H = 4.52.

$\text{C}_{13}\text{H}_{15}\text{O}_5$  requires C = 62.90; H = 4.84 per cent.

This substance, which it is proposed to name *excoecarin*, crystallises in glistening, lemon-yellow needles, sparingly soluble in cold alcohol or ether, insoluble in benzene or chloroform; when heated, it becomes orange-coloured at  $210^\circ$  and melts with effervescence at  $219\text{--}221^\circ$ . It is soluble in aqueous and alcoholic alkaline solutions with a beautiful, violet-red coloration, which is bluer in the latter case, and in ammonia to form a red-brown liquid, and these solutions, on exposure to air, are rapidly oxidised and assume a rich brown tint. With alcoholic lead acetate, no precipitate is formed, and it yields neither acid compounds with mineral acids nor insoluble salts with alcoholic potassium or sodium acetates. Sulphuric acid dissolves it with a brown, and nitric acid with an orange-yellow, tint, but alcoholic ferric chloride gives no coloration.

Although it does not dye calico with or without mordants, it has a weak, although decided, affinity for animal fibres, the best results being obtained by employing 10 per cent. of the colouring matter in conjunction with 5 per cent. of tartaric or oxalic acid. The shade produced is a pure pale yellow, but the bath is not exhausted, and the result, though scientifically interesting, is of no technical value.

When examined by Zeisel's method, it was found that *excoecarin* does not contain a methoxy-group. When digested with acetic an-

hydride and sodium acetate in the usual manner, a viscous, readily soluble product is obtained which could not be obtained in a crystalline condition.

The *benzoyl* compound was first prepared according to Baumann and Schotten's method, but owing to the readiness with which the alkaline solution of the colouring matter is oxidised, the yield was poor. The substance was therefore heated at 175—185° with ten times its weight of benzoic anhydride for 5 hours and the mixture poured into alcohol. A colourless precipitate separated overnight, and this was collected, washed with alcohol, and purified by crystallisation, first from alcohol and finally from a mixture of alcohol and acetic acid :

0.1110 gave 0.2963 CO<sub>2</sub> and 0.0439 H<sub>2</sub>O. C = 72.79 ; H = 4.39.

0.1105 „ 0.2959 CO<sub>2</sub> „ 0.0445 H<sub>2</sub>O. C = 73.03 ; H = 4.47.

0.1112 „ 0.2968 CO<sub>2</sub> „ 0.0445 H<sub>2</sub>O. C = 72.79 ; H = 4.44.

C<sub>18</sub>H<sub>9</sub>O<sub>5</sub>(C<sub>7</sub>H<sub>5</sub>O)<sub>2</sub> requires C = 72.85 ; H = 4.28 per cent.

It consisted of colourless needles melting at 168—171°, sparingly soluble in boiling alcohol, more readily in boiling acetic acid, insoluble in dilute alkalis. In one operation, this compound was contaminated with a trace of a more sparingly soluble product melting at 209—211°, probably a lower benzoyl derivative, for the compound melting at 168—171° was not altered by further treatment with benzoic anhydride.

*Fusion with Alkali.*—Excoecarin was heated with twelve times its weight of caustic potash and a little water at 200—220° for half an hour. The rich brown fused mass was poured into water, neutralised with acid, extracted with ether, and the extract evaporated to dryness. The dark-coloured oil, which on standing became crystalline, was dissolved in water, excess of sodium bicarbonate added, and extracted with ether (A), and the aqueous residue neutralised with acid and extracted with ether (B).

(A) yielded a crystalline residue, which was purified by crystallisation from benzene with the aid of animal charcoal :

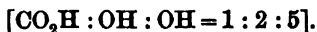
0.0779 gave 0.1928 CO<sub>2</sub> and 0.0438 H<sub>2</sub>O. C = 67.49 ; H = 6.24.

C<sub>7</sub>H<sub>8</sub>O<sub>2</sub> requires C = 67.74 ; H = 6.45 per cent.

It formed colourless leaflets melting at 121—123°, readily soluble in water. The alkaline solution becomes brown on standing in air. Suspecting this to be a hydroquinone derivative, its aqueous solution was treated with ferric chloride and digested at the boiling temperature for a short time. The solution was extracted with ether, the extract evaporated, and the residue sublimed between watch glasses. The product formed golden-yellow leaflets melting at 68° and having the reactions of *toluquinone* [CH<sub>3</sub>:O:O=1:2:5]



(Nietzki, *Ber.*, 1877, 10, 833). Substance A was therefore the corresponding *hydrotoluquinone*, for which Nietzki gives the melting point 124°. B gave a dark-coloured, syrupy residue from which crystals separated on long standing. This was dissolved in water, the solution saturated with salt, filtered from the black, tarry precipitate, the filtrate extracted with ether, and the extract evaporated. The residue, on crystallisation from benzene, yielded colourless needles melting at 199—200°, which, with aqueous ferric chloride, gave a deep blue coloration. When distilled, a purple vapour was evolved and a crystalline product condensed which melted at 150—155°; this was dissolved in water, the solution treated with sodium bicarbonate, extracted with ether, and the purified substance crystallised from benzene with the aid of animal charcoal. It gave no coloration with aqueous ferric chloride, melted at 166—168°, and was evidently *hydroquinone*. Substance B was consequently *hydroquinonecarboxylic* (*hydroxysalicylic*) acid



It seemed probable that this acid was derived from the action of the alkali upon the hydrotoluquinone first produced, and to determine this, some quantity of the phenol prepared from *o*-toluidine was heated with caustic potash under conditions similar to those previously employed. Although a considerable proportion of the substance remained unattacked, some *hydroquinonecarboxylic* acid was produced, and its presence above, at least in part, must have originated from the hydrotoluquinone.

*Action of Bromine.*—Attempts to prepare a bromine derivative of excoecarin were unsuccessful, as decomposition so readily ensued, but experiments in the following manner lead to the isolation of a new product.

Two grams of the substance, dissolved in 25 c.c. of a half-saturated solution of potassium acetate in absolute alcohol, were cooled in a freezing mixture and bromine added drop by drop until the mixture, at first green, developed an orange-red coloration. The resulting semisolid, crystalline mass was collected on the pump, washed with a little absolute alcohol, then with water, and finally with alcohol. This substance on standing over sulphuric acid gradually darkened, and on drying at 100° became olive-green, but it was ascertained that this colour change was not a decomposition. The yield was 1.65 grams. It was finally purified by crystallisation from nitrobenzene:

0.1127 gave 0.2608  $\text{CO}_2$  and 0.0435  $\text{H}_2\text{O}$ . C = 63.10; H = 4.28.

0.1081 „ 0.2506  $\text{CO}_2$  „ 0.0400  $\text{H}_2\text{O}$ . C = 63.22; H = 4.10.

$\text{C}_{13}\text{H}_{10}\text{O}_5$  requires C = 63.41; H = 4.06 per cent.

Thus obtained, it formed flat, copper-coloured needles or leaflets

sparingly soluble in alcohol and melting with decomposition at about  $250^{\circ}$ . Caustic alkalis dissolve it with a brown tint which, on standing in air, becomes first olive-green, and finally brownish-black. This substance, which it is proposed to name *excoecarone*, has the composition of excoecarin less  $2\text{H}$ , and as the latter has been shown to contain a hydroquinone group, the above reaction most probably consists in the oxidation of this to a quinone nucleus. The following experiment supports this view.

*Reduction of Excoecarone.*—A boiling aqueous solution of the substance was treated with sodium bisulphite, and the digestion continued until a sample of the liquid, on addition of alkali, gave a violet-red coloration. It was then acidified, extracted with ether, the extract well washed with water, and evaporated to a small bulk. On addition of chloroform, yellow crystals separated, which, after purification, melted at  $219\text{--}221^{\circ}$ , and had all the properties of *excoecarin*.

*Action of Quinone.*—Addition of excess of quinone to a boiling alcoholic solution of excoecarin caused the formation of a deep brown liquid, which after a few minutes' digestion was allowed to cool. Crystals of a deep green colour gradually separated, and these were collected, washed with alcohol, and crystallised from the same solvent:

0.1125 gave 0.2609  $\text{CO}_2$  and 0.0420  $\text{H}_2\text{O}$ .  $\text{C} = 63.24$ ;  $\text{H} = 4.14$ .

$\text{C}_6\text{H}_4\text{O}_2 \cdot \text{C}_{18}\text{H}_{12}\text{O}_5$  requires  $\text{C} = 64.04$ ;  $\text{H} = 4.49$  per cent.

Thus obtained, the product formed minute, green-coloured leaflets melting at  $190^{\circ}$  with decomposition. Its alcoholic solution is deep brown, and alkalis dissolve it with a coloration similar to that of *excoecarone*. When digested with boiling sodium bisulphite solution, it yields *excoecarin* melting at  $219\text{--}221^{\circ}$ . Although complete proof is wanting and could not be obtained owing to lack of raw material, it is considered probable that this substance is of the nature of quinhydrone, the hydroquinone nucleus of the *excoecarin* reacting with the quinone. Its similarity in certain points to *excoecarone*, on the other hand, made it possible that it consisted of this substance contaminated with a trace of some impurity not readily removed by the methods employed.

*Methylation of Excoecarin.*—Five grams of the substance were dissolved in 100 c.c. of methyl alcohol and treated with 20 c.c. of methyl iodide. To the boiling liquid, a solution of 4.5 grams of caustic potash in methyl alcohol was added, drop by drop, at intervals extending over three days, this procedure having for its object to prevent as far as possible the oxidation of the alkaline solution of the colouring matter. The product was evaporated to a small bulk, poured into ether, and the solution washed with dilute alkali. The pale yellow, ethereal liquid, which had a strong green fluorescence, was evaporated, and the viscous residue dissolved in carbon disulphide and left overnight.

Crystals gradually separated which were collected and recrystallised two or three times with a mixture of benzene and carbon disulphide. The mother liquor contained some quantity of an uncrystallisable resin :

0.1126 gave 0.2694  $\text{CO}_2$  and 0.0600  $\text{H}_2\text{O}$ .  $\text{C} = 65.25$  ;  $\text{H} = 5.92$ .

0.1037 „ 0.1830  $\text{AgI}$ .  $\text{CH}_3 = 11.26$ .

0.1077 „ 0.1890  $\text{AgI}$ .  $\text{CH}_3 = 11.20$ .

0.1222 „ 0.2115  $\text{AgI}$ .  $\text{CH}_3 = 11.04$ .

$\text{C}_{13}\text{H}_{10}\text{O}_5(\text{CH}_3)_2$  requires  $\text{C} = 65.21$  ;  $\text{H} = 5.80$  ;  $\text{CH}_3 = 10.87$  per cent.

This compound was very troublesome to prepare, at first nothing but the resin being obtained, due evidently to the too rapid addition of the alkali, but subsequently yields varying from 0.8 to 1.1 grams of the crystalline ether were obtained.

It formed glistening, yellow needles melting at  $117-119^\circ$ , very readily soluble in alcohol, sparingly in hot carbon disulphide, and is characterised by the deep green fluorescence of its solutions. Alkaline solutions do not dissolve it, and alcoholic ferric chloride gives no coloration. With sulphuric acid, it gives a deep reddish-brown liquid, which on addition of a drop of nitric acid becomes blue-violet, and finally orange coloured. When dissolved in nitric acid of sp. gr. 1.54 and the solution evaporated to a small bulk, a crystalline product separates on cooling, consisting of oxalic acid and a compound readily soluble in benzene. The latter crystallises in needles, and is apparently a nitro-compound, but the yield was too small to permit of its investigation. As excoecarin contains three hydroxyl groups but yields only a dimethyl ether, it would appear to contain one hydroxyl in the ortho-position to a carbonyl group. Attempts to prepare an acetyl compound in a crystalline condition were unsuccessful, the product consisting of an orange-yellow resin ; a similar result was obtained in an attempt to prepare a benzoyl derivative.

Experiments carried out on the ethylation of excoecarin gave a viscous substance, from which, after standing some weeks, a small amount of crystalline matter separated ; owing, however, to its soluble nature, the yield of substance was too small to admit of examination.

*Molecular Weight of Excoecarin.*—For this purpose, the dimethyl ether was employed with the following result :

0.4146 dissolved in 14.468 acetic acid depressed the freezing point  $0.385^\circ$ . Found, 287.

0.4090 dissolved in 13.380 acetic acid depressed the freezing point  $0.420^\circ$ . Found, 283.

This corresponds with the formula  $\text{C}_{13}\text{H}_{10}\text{O}_5(\text{CH}_3)_2 = 276$ , and excoecarin itself has thus the formula  $\text{C}_{13}\text{H}_{12}\text{O}_5$ .

*Summary.*—The investigation of excoecarin shows that this colouring matter contains three hydroxyl groups, one of which is not methylated, and that by means of fused alkali it gives hydrotoluquinone and hydroquinonecarboxylic acid, the latter being derived in part, if not entirely, from the former. Oxidation with bromine gives excoecarone,  $C_{18}H_{10}O_5$ , which, by reduction, is reconverted into excoecarin, and treatment with quinone yields a compound which is probably a quinhydrone compound of the formula  $C_{19}H_{16}O_7$ . The latter results indicate the presence in the colouring matter of free hydroquinone hydroxyls. Any further clue to its constitution has not yet been obtained, though this is probably of a nature not previously met with among the natural colouring matters. Interesting results would, no doubt, ensue by a study of the oxidation products of the dimethyl ether, but the laborious operations involved in the preparation of any quantity of this substance will render the work extremely slow and difficult.

*The Colouring Matter A* (p. 211).

The crude product was purified by two or three crystallisations from alcohol with the aid of animal charcoal.

0.1099 gave 0.2600  $CO_2$  and 0.0465  $H_2O$ . C = 64.51; H = 4.70.

$C_{14}H_{12}O_5$  requires C = 64.61; H = 4.61 per cent.

This colouring matter, which it is proposed to name *jacarandin*, crystallises in glistening, yellow plates or leaflets which commence to darken at  $220^\circ$  and melt with evolution of gas at  $243$ – $245^\circ$ . It is sparingly soluble in alcohol and the usual solvents to form pale yellow liquids having a green fluorescence, and soluble in sulphuric acid with a deep orange coloration having a strong green fluorescence. With caustic alkali solutions, it gives orange-red liquids; with alcoholic lead acetate, a bright orange-coloured precipitate; and with alcoholic ferric chloride, a dark greenish-black solution. When examined by Zeisel's method, it was found not to contain a methoxy-group.

It dyes mordanted fabrics good full shades, the following being obtained with mordanted wool:

Chromium.	Aluminium.	Tin.	Iron.
Dull yellow-brown.	Orange-brown.	Bright golden-yellow.	Deep olive.

These somewhat resemble those given by luteolin, but are rather more orange. It has a slight affinity for animal fibres, pale yellow shades being obtained, which are, however, feebler than those given by excoecarin.

When treated with mineral acids in the presence of acetic acid, no crystalline compounds separate, but with alcoholic potassium acetate a potassium salt is formed. Analysis of this compound did not give

concordant results, owing to the sparingly soluble nature of the colouring matter, the small portion unattacked separating together with the salt on cooling the mixture.

*Acetyl compound.*—This substance was digested with six parts of acetic anhydride and one of anhydrous sodium acetate at the boiling point for one hour. On pouring into water, a pale yellow, crystalline precipitate separated which was purified by recrystallisation from alcohol.

0.1166 gave 0.2667  $\text{CO}_2$  and 0.0489  $\text{H}_2\text{O}$ .  $\text{C} = 62.37$ ;  $\text{H} = 4.65$ .

0.1211 „ 0.2775  $\text{CO}_2$  „ 0.0535  $\text{H}_2\text{O}$ .  $\text{C} = 62.49$ ;  $\text{H} = 4.86$ .

$\text{C}_{14}\text{H}_{10}\text{O}_5(\text{C}_2\text{H}_3\text{O})_2$  requires  $\text{C} = 62.79$ ;  $\text{H} = 4.65$  per cent.

It formed pale yellow needles sparingly soluble in alcohol and melting at  $192\text{--}194^\circ$ . An attempt to determine the acetyl groups in the usual way, by decomposing the acetyl derivative with sulphuric acid, gave 72.23 per cent. of regenerated colouring matter, but a slight decomposition of the latter had ensued, as a resinous substance was also present. It has been found by one of us that some acetyl derivatives are decomposed by digestion with a boiling alcoholic solution of potassium acetate, and quantitative experiments are now being carried out to determine if this method is of general application, not only with acetyl, but also with benzoyl, compounds. Such a process would be valuable with colouring matters which cannot withstand the action of strong acids. As colouring matters of the nature of quercetin yield in this manner the mono-potassium salt, this reaction was applied to acetyljacarandin, not only to determine the acetyl groups, but with the hope of producing a potassium salt which would give some clue to its molecular weight. A weighed quantity of the acetyl compound was therefore dissolved in boiling absolute alcohol, treated with excess of alcoholic potassium acetate, and the solution slowly evaporated. As soon as crystals commenced to separate, the mixture was left for a few minutes, the potassium salt collected, washed with methyl alcohol, dried at  $160^\circ$ , weighed, and analysed. The filtrate and washings were again evaporated, cautiously diluted with boiling water containing a few drops of hydrochloric acid, and the crystals of the colouring matter which separated collected when the mixture was cold, and weighed. Three distinct preparations of the salt were made, and two acetyl determinations carried out:

0.3857 gave 0.0607  $\text{K}_2\text{SO}_4$ .  $\text{K} = 7.05$ .

0.4295 „ 0.0665  $\text{K}_2\text{SO}_4$ .  $\text{K} = 6.94$ .

0.7495 „ 0.1180  $\text{K}_2\text{SO}_4$ .  $\text{K} = 7.05$ .

$\text{C}_{23}\text{H}_{23}\text{O}_{10}\text{K}$  requires  $\text{K} = 6.99$ .

It formed glistening, yellow needles, insoluble in cold water, somewhat soluble in alcohol.

*Acetyl Determinations.*

1·4140 gave 1·0682 colouring matter. Found 75·54.

1·8907 „ 1·4141 „ „ „ 74·82.

$C_{14}H_{10}O_6(C_2H_5O)_2$  requires  $C_{14}H_{12}O_5 = 75·58$  per cent.

These results indicate that the molecular weight of jacarandin is probably represented by the formula  $C_{14}H_{12}O_5$ , and that it gives a diacetyl compound,  $C_{14}H_{10}O_6(C_2H_5O)_2$ . Its potassium salt, prepared in the manner already described, and formed by the replacement of one hydrogen in a double molecule of the colouring matter, will thus be analogous to those of rhamnetin and rhamnazin (Trans., 1899, 75, 433).

The *benzoyl* derivative was prepared by heating the colouring matter to 180° for 4 hours with ten times its weight of benzoic anhydride and pouring the product into alcohol. Yellow, prismatic needles slowly separated, and, after being left overnight, were collected and purified by crystallisation from a mixture of alcohol and acetic acid. It melted at 167—169°:

0·1121 gave 0·2952  $CO_2$  and 0·0428  $H_2O$ . C = 71·82; H = 4·24.

$C_{14}H_{10}O_6(C_7H_5O)_2$  requires C = 71·79; H = 4·27 per cent.

Experiments on the *methylation* of jacarandin gave a large amount of resinous matter and also a trace of a crystalline ether too small in quantity for analysis. The latter forms bright yellow needles, readily soluble in boiling alcohol, soluble in sulphuric acid, forming an orange liquid which has a deep green-coloured fluorescence. It melts at 154—155°. The paucity of raw material did not permit of further work in this direction, but it is possible that under altered conditions a larger yield of the ether could be obtained.

Fusion of a trace with alkali at 200—220° yielded a very soluble acid, which gave a green coloration with ferric chloride, but was not identical with protocatechuic acid. The presence of a fatty acid, possibly acetic acid, was also detected.

Unless a more plentiful source of this colouring matter be discovered, but little insight can be obtained into its constitution. Of the known natural colouring matters, it approaches in general properties most closely to curcumin, but its molecular weight (curcumin,  $C_{21}H_{20}O_6$ , Ciamician and Silber, *Ber.*, 1897, 30, 192) does not accord with this supposition. Possibly, therefore, it is a member of some group hitherto unknown.

The *resin* A (p. 211) was obtained as an orange-brown, transparent, brittle mass, resembling jacarandin in many of its properties. It contained some quantity of this colouring matter, and as no method has been at present devised by which this can be entirely removed, it

has not been closely examined. It dyes mordanted calico similarly, but not so strongly as jacarandin, but there can be no doubt that to this substance the tinctorial properties of green ebony are mainly due. The yield was approximately 0.1 per cent.

The resin B (p. 212) in appearance resembles the resin A, but it does not dye mordanted calico. Its reactions coincided with those of excorearin, with which no doubt it was to some extent contaminated. It is the main constituent of green ebony, and was present in one sample to the extent of 0.4 per cent.

### *Dyeing Properties of Green Ebony.*

These experiments corroborated those of Bancroft (*loc. cit.*) in that the shades given by green ebony are of a similar character to those obtained with old fustic. The colours, however, from the former with aluminium, tin, and copper mordants are browner, and with iron greener and paler, than those yielded by old fustic. Employing mordanted woollen cloth, the following shades were produced :

Chromium.	Aluminium.	Tin.	Copper.	Iron.
Dull yellow-brown.	Dull brown-yellow.	Golden-yellow.	Pale brown.	Olive-green.

With 40 per cent. of the dyewood, the iron mordant gives greener and brighter tints than with larger amounts, in which case a browner colour is produced. Possibly from this green shade and the extremely hard and compact nature of the wood, the name "green ebony" has originated. The sample of wood here employed possessed half the colouring power of an average sample of old fustic.

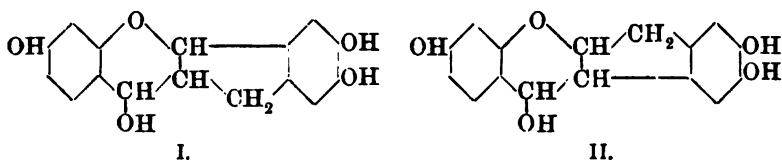
In the earlier stages of this work, which has been in progress for more than two years, considerable assistance was given by Mr. R. Gloag Thomson, of Perth, to whom we are much indebted. The authors also express their thanks to the Research Fund Committee of the Chemical Society for a grant which has been in part employed to cover the expenses of the research.

CLOTHWORKERS' RESEARCH LABORATORY,  
DYEING DEPARTMENT,  
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XXIII.—On *Brazilic Acid* and the Constitution of *Brazilin*.

By W. H. PERKIN, jun.

IN Part I. of this research (A. W. Gilbody, W. H. Perkin, jun., and J. Yates, *Trans.*, 1901, 79, 1401), it was argued that since trimethylbrazilin, on oxidation with permanganate, yields 2-carboxy-5-methoxyphenoxycetic acid and *metahemipinic acid*, the constitution of brazilin must be represented by one of the following formulæ:



These two formulæ are so similar that for a long time it was found impossible to obtain evidence sufficient to afford even a clue as to which was the correct one, but ultimately the detailed examination of *brazilic acid* (*loc. cit.*, p. 1410) led to results which show clearly that formula I is to be accepted as representing the constitution of brazilin.

*Brazilic acid*,  $C_{12}H_{12}O_6$ , which is produced in a yield of only 0.7 per cent. by the oxidation of trimethylbrazilin with permanganate, crystallises from water in colourless needles and melts at  $129^\circ$ ; it is a monobasic acid, since its silver salt has the formula  $C_{12}H_{11}AgO_6$ , and its sodium salt the formula  $C_{12}H_{11}NaO_6$ ; when, however, its solution in water is boiled with baryta, it yields a barium salt of the formula  $C_{12}H_{10}BaO_6$ , and therefore, under these circumstances, it behaves like a dibasic acid, a point which will be referred to later.

Brazilic acid contains 1 methoxy-group, as shown by Zeisel's method, and when fused with potash, it is decomposed with formation of a readily soluble acid which in aqueous solution gives an intense violet coloration with ferric chloride; it is therefore derived from the resorcylic nucleus in brazilin.

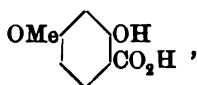
On treatment with hydroxylamine, brazilic acid yields an oxime, and with semicarbazide, a semicarbazone; it therefore contains a carbonyl group, and this group is evidently situated in the  $\gamma$ -position to the carboxyl group, because, when reduced with sodium amalgam, brazilic acid yields *dihydrobrazilic acid*,  $C_{12}H_{14}O_6$ , and this, when liberated from its sodium salt, spontaneously loses water with formation of the lactone  $C_{12}H_{12}O_5$ .

These facts, although they throw much light on the constitution of brazilic acid, are not sufficient to establish its formula, but the neces-



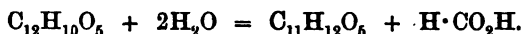
sure further information was ultimately obtained by the examination of the behaviour of the acid with dehydrating agents, especially sulphuric acid. When brazilic acid is warmed with concentrated sulphuric acid, it loses 1 molecule of water and is converted into *anhydrobrazilic acid*, a crystalline substance which melts at  $197^{\circ}$ , and differs sharply from brazilic acid in being very sparingly soluble even in boiling water.

This new acid is monobasic and still contains a carbonyl group, since with hydroxylamine it yields a crystalline oxime,  $C_{12}H_{11}O_6N$ ; furthermore, a determination by Zeisel's method showed that it still contained the methoxy-group which was present in the brazilic acid. It is also an unsaturated acid, because its solution in sodium carbonate at once decolorises permanganate, and on investigating this oxidation it was found that an almost quantitative yield of *p-methoxysalicylic acid*,

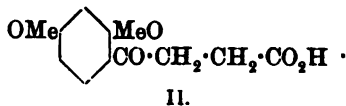
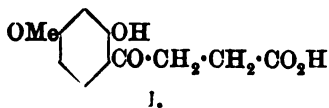


is formed if the oxidation is carried on at a sufficiently low temperature, a fact which affords a valuable clue as to the constitution of the acid.

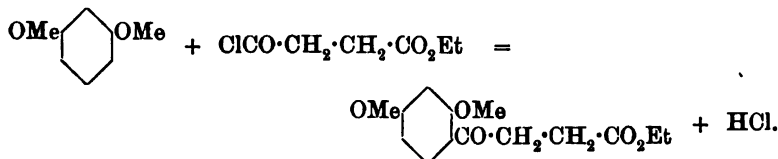
A further clue was obtained by the discovery that, when boiled with baryta water, anhydrobrazilic acid is readily decomposed into formic acid and a new acid,  $C_{11}H_{12}O_6$ , thus:



This new acid crystallises from water in colourless needles and melts at  $155^{\circ}$ ; it is a monobasic, ketonic acid and its aqueous solution gives, with ferric chloride, an intense violet coloration. Since anhydrobrazilic acid gives no coloration with ferric chloride, it was probable that the elimination of formic acid had been accompanied by the formation of a free hydroxyl group in the benzene ring. That this is the case was proved by the fact that the methyl ester of the acid  $C_{11}H_{12}O_6$ , when heated with sodium methoxide and methyl iodide, is converted into the methyl ester of an acid,  $C_{12}H_{14}O_6$ , which gives no coloration with ferric chloride; the hydroxy-group of the former acid had therefore been converted into a methoxy-group in the latter. The further consideration of the properties of the acid  $C_{11}H_{12}O_6$ , taken in conjunction with the fact that anhydrobrazilic acid on oxidation yields *p-methoxysalicylic acid*, seemed to indicate that the acid  $C_{11}H_{12}O_6$  is 6-hydroxy-4-methoxybenzoylpropionic acid (I), and that its methyl derivative,  $C_{12}H_{14}O_6$ , is therefore dimethoxybenzoylpropionic acid (II),



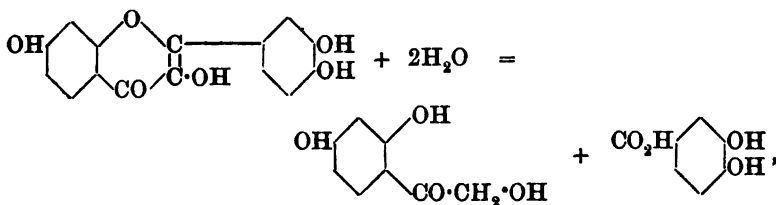
In order to prove this point, it was decided to attempt the synthesis of the dimethoxy-acid, and after a number of failures this was ultimately accomplished (in conjunction with Mr. E. Ormerod) by treating a mixture of dimethylresorcinol and the ester of the half-chloride of succinic acid with aluminium chloride, thus :



The product of this reaction yielded, on hydrolysis, an acid melting at  $147^\circ$ , which was identical with the dimethoxy-acid,  $\text{C}_{12}\text{H}_{14}\text{O}_5$ , obtained from brazilin, and the constitutions of this acid and of the hydroxy-methoxy-acid,  $\text{C}_{11}\text{H}_{12}\text{O}_5$ , from which it was obtained are consequently proved to be represented by the formulæ II and I given above.

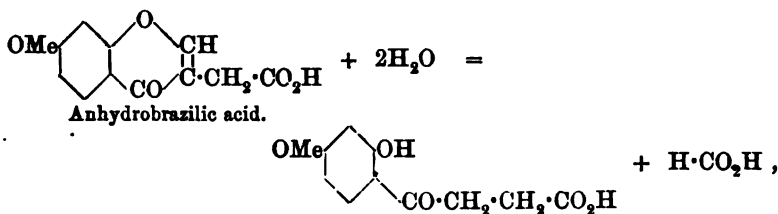
Referring again to the conversion of anhydrobrazilic acid by hydrolysis with baryta into hydroxymethoxybenzoylpropionic acid and formic acid,  $\text{C}_{12}\text{H}_{10}\text{O}_5 + 2\text{H}_2\text{O} = \text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} + \text{H} \cdot \text{CO}_2\text{H}$ , we see that we have here a case of a decomposition which has repeatedly been observed in the *pheno-γ-pyrone* series.

Thus fisetin, which is somewhat similarly constituted to brazilin, when digested with alcoholic potash is decomposed into fisetol and protocatechuic acid,



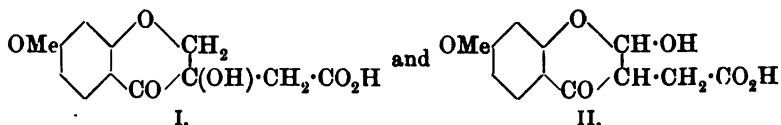
and many other similar examples might be given.

Arguing, then, from analogy, it is evident that the formula of *anhydrobrazilic acid* and its decomposition into methoxyhydroxybenzoylpropionic acid must be represented thus :



and this formula is in accordance with all the properties of the acid.

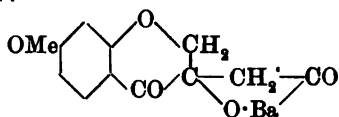
Since, then, anhydrobrazilic acid is produced from brazilic acid by the elimination of 1 molecule of water and consequent formation of a double-linking, it follows that there are only two formulæ which can represent brazilic acid, namely,



In formula II, the hydroxyl group is in the  $\gamma$ -position in relation to the carboxyl group, and an acid of this constitution should therefore readily yield a lactone, whereas an acid, represented by formula I, being a  $\beta$ -hydroxy-acid, would not show any tendency to lactone formation.

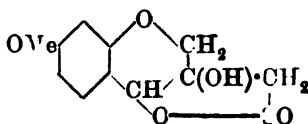
Since brazilic acid is not only stable at  $100^\circ$ , but even when boiled with hydrochloric acid shows no tendency to pass into a lactone, its constitution must obviously be represented by formula I.

It has been shown by the preparation and analysis of its sodium, silver, and barium salts that brazilic acid is a well-characterised, monobasic acid, but it is also pointed out (p. 228) that when boiled with baryta water it yields a very sparingly soluble barium salt of the formula  $C_{12}H_{10}O_6Ba$ , which is quite different from the normal salt,  $(C_{12}H_{11}O_6)_2Ba$ , obtained by precipitating the solution of the sodium salt with barium chloride. The formation of the salt  $C_{12}H_{10}BaO_6$  is evidently due to the hydrogen of the hydroxyl group, as well as that of the carboxyl group, being replaceable by barium, that is to say, the salt has the constitution :

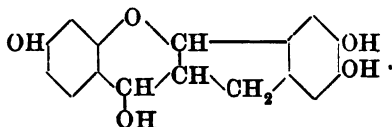


That the hydrogen of this hydroxyl group should be replaceable by treatment with caustic alkalis is not surprising in view of its proximity to the CO group of the dihydropyrone ring.

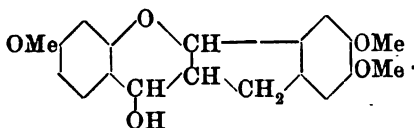
When brazilic acid is reduced by sodium amalgam, it is converted into the lactone of dihydrobrazilic acid, and the constitution of this substance must therefore be represented thus :



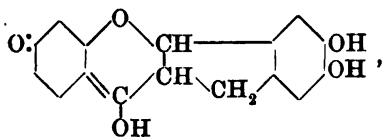
If, now, the two formulæ for brazilin given at the beginning of this paper be examined, it will be seen that only formula I can yield brazilic acid in a simple manner, and there seems, therefore, to be no reason to doubt that the constitution of brazilin is:



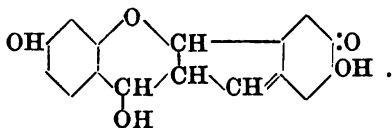
This formula accounts for all the known properties of brazilin in a satisfactory manner, and of the four hydroxyl groups three are represented as phenolic and the other one as alcoholic; it is thus obvious that three only should be converted into methoxy-groups on treating brazilin with sodium methoxide and methyl iodide, and this is actually the case. The trimethylbrazilin so produced, which has been so largely employed in this investigation, will have the constitution:



In the previous paper (*loc. cit.*, p. 1403), it was suggested that the constitution of the dye-stuff, *brazilein*,  $C_{16}H_{12}O_5$ —which contains two atoms of hydrogen less than brazilin and is produced from it by oxidation—may probably be:



the two atoms of hydrogen being removed, one from the  $CH(OH)$  group and one from the  $OH$  group of the resoreyl nucleus. It must, however, be pointed out that it is quite possible that the two atoms of hydrogen may be derived from the  $CH_2$  group and the parahydroxy-group of the catechol nucleus, and the formula of brazilein would then be:



Since, however, *brazilein* yields such complicated, salt-like compounds with sulphuric acid (A. G. Perkin and Hummel, *Ber.*, 1882, 15, 2343), it

is not improbable that it may be derived from several molecules of brazilin, and therefore have a constitution much more complex than represented by the formulæ given above. This view receives some support from the fact that it has so far not been found possible to reconvert brazilein into brazilin by reduction.

*Brazilic Acid,  $C_{12}H_{12}O_6$ .*

This acid was mentioned in the previous paper (Trans., 1901, 79, 1411), and the method employed in isolating it from the products of the oxidation of trimethylbrazilin with potassium permanganate was briefly described. Two analyses were also given, the mean of which ( $C=57.1$ ;  $H=5.0$ ) agrees with the numbers required by the formula  $C_{12}H_{12}O_6$  ( $C=57.2$ ;  $H=4.8$ ). The molecular weight of the acid has since been determined by the cryoscopic method, when two experiments gave 265 and 276, whereas the molecular weight of  $C_{12}H_{12}O_6$  is 254.

*Brazilic acid* melts at  $129-130^\circ$  and is only sparingly soluble in cold water; it dissolves readily in hot water and separates, on slowly cooling, in long, colourless needles. It dissolves readily in alcohol, ether, or acetic acid, but less readily in chloroform, and is almost insoluble in cold light petroleum; in hot benzene, it is readily soluble, and separates, on cooling, in long needles. That brazilic acid is a saturated substance is shown by the fact that its solution in cold sodium carbonate does not decolorise permanganate, oxidation taking place, indeed, only very slowly on warming. Bromine dissolved in chloroform is also without action on the acid in the cold. An aqueous solution of brazilic acid gives no coloration with ferric chloride, but when fused with potash the acid is readily decomposed, and, on acidifying and extracting with ether, a syrupy substance is obtained which is very soluble in water and gives, with ferric chloride, an intense violet coloration.

When boiled with acetic anhydride, brazilic acid dissolves, forming a yellow solution, but this rapidly becomes brown and then quite black, decomposition evidently taking place. If a small quantity of the dry acid is heated in a test-tube, it chars and gives an oily distillate which has a strong odour of coumarin.

Brazilic acid contains one methoxy-group, as is shown by the following determinations made by Zeisel's method:

0.1429 gave 0.1370 AgI.  $OCH_3 = 12.6$ .

0.1892 „ 0.1795 AgI.  $OCH_3 = 12.5$ .

$C_{12}H_{12}O_6$ , containing one  $OCH_3$ , requires  $OCH_3 = 12.3$  per cent.

The residues from these methoxy-determinations were decolorised by sulphurous acid and extracted with ether, when a substance was

obtained which crystallised from water in pale yellow crystals and melted at about  $178^{\circ}$ ; it was not further examined.

*Salts of Brazilic Acid.*—That this acid is monobasic was first proved by titration with decinormal sodium hydroxide, using phenolphthalein as the indicator.

0.21 gram, dissolved in warm water, required for neutralisation 8.1 c.c. of sodium hydroxide solution = 0.0324 gram, whereas this amount of an acid,  $C_{12}H_{11}O_6$ , if monobasic, would neutralise 0.033 gram NaOH.

The solution was then mixed with a further quantity of 11.9 c.c. of the sodium hydroxide (making 20 c.c. in all) and boiled for 5 minutes, when, on titrating back, it was found that the amount neutralised was practically the same as before, namely, 0.034 gram.

The *sodium* salt,  $C_{12}H_{11}O_6Na$ , separates in glistening plates when a hot solution of the acid is neutralised with sodium carbonate and then allowed to cool. The salt was recrystallised from water, dried at  $100^{\circ}$ , and analysed:

0.1602 gave 0.0405  $Na_2SO_4$ .  $Na = 8.2$ .

$C_{12}H_{11}O_6Na$  requires  $Na = 8.4$ .

This salt, which does not appear to contain water of crystallisation, is comparatively sparingly soluble in cold water, although it dissolves readily on warming. On account of the facility with which it crystallises even when impure, it proved to be very valuable as a means of isolating brazilic acid from mixtures with other acids and resinous products. The corresponding potassium salt appears to be readily soluble in water.

The *silver* salt,  $C_{12}H_{11}O_6Ag$ , is obtained, on adding silver nitrate to a neutral solution of the ammonium salt, as a white precipitate which is very sparingly soluble in water. On analysis

0.1613 gave 0.2352  $CO_2$ , 0.0496  $H_2O$ , and 0.0484 Ag.  $C = 39.8$ ;  
 $H = 3.4$ ;  $Ag = 30.1$ .

0.201 gave 0.2932  $CO_2$ , 0.0608  $H_2O$ , and 0.0605 Ag.  $C = 39.8$ ;  
 $H = 3.3$ ;  $Ag = 30.1$ .

$C_{12}H_{11}O_6Ag$  requires  $C = 40.1$ ;  $H = 3.1$ ;  $Ag = 30.1$  per cent.

The *barium* salt,  $(C_{12}H_{11}O_6)_2Ba \cdot 2H_2O$ .—When a neutral solution of the ammonium salt of brazilic acid is mixed with barium chloride, an amorphous, almost gelatinous, precipitate is at first produced, but this rapidly becomes crystalline. This salt is readily soluble in hot water, and separates, on cooling, in slender needles; after draining on porous porcelain and exposing to the air for 3 days, it appears to contain 2 molecules of water of crystallisation:

0.2228 air-dried salt lost, at  $100^{\circ}$ ,  $0.0118 = 5.3$ .

$(C_{12}H_{11}O_6)_2Ba, 2H_2O$  requires 5.3 per cent. of water.

0.211, dried at  $100^{\circ}$ , gave 0.0773  $BaSO_4$ . Ba = 21.6.

$(C_{12}H_{11}O_6)_2Ba$  requires Ba = 21.7 per cent.

A neutral solution of the ammonium salt of brazilic acid gives no precipitate with calcium chloride, a pale blue precipitate with copper sulphate, and a white, amorphous, very insoluble precipitate with lead acetate.

The barium salt,  $C_{12}H_{10}O_6Ba$ , the constitution of which is discussed in the introduction to this paper, was prepared as follows.

A hot solution of brazilic acid was rapidly mixed with a large excess of hot baryta water, when a white, granular precipitate rapidly separated and increased, apparently, on boiling. After boiling for a few minutes out of contact with air, the salt was rapidly collected on the pump, washed repeatedly with boiling water, dried at  $100^{\circ}$ , and analysed:

0.4653 gave 0.2689  $BaSO_4$ . Ba = 34.0.

0.1449 „ 0.0824  $BaSO_4$ . Ba = 33.5.

$C_{12}H_{10}O_6Ba$  requires Ba = 35.5.

$C_{12}H_{10}O_6Ba, H_2O$  requires Ba = 33.9 per cent.

These results, which agree better with the latter formula, clearly show that brazilic acid, when boiled with baryta, yields a dibasic barium salt. In order to be certain that no change in constitution had taken place during this treatment, the barium salt was ground in a mortar with a little dilute hydrochloric acid, and the crystalline precipitate collected on the pump, washed with water, and dried at  $100^{\circ}$ . It then melted at  $129^{\circ}$  and consisted of pure brazilic acid.

*Oxime of Brazilic Acid*,  $C_{12}H_{13}O_6N$ .—In preparing this oxime, the pure acid (0.5 gram) was dissolved in dilute caustic potash (containing 2 grams KOH), a solution of 2 grams of hydroxylamine hydrochloride was then added, and the whole allowed to stand for 24 hours. On acidifying, a flocculent precipitate separated; this was extracted with ether, the ethereal solution dried over calcium chloride and evaporated, and the syrupy residue left over sulphuric acid in a vacuum desiccator for several days, when it gradually solidified. As all attempts to recrystallise the substance were unsuccessful, it was analysed in its crude form:

0.2376 gave 12.1 c.c. nitrogen at  $22^{\circ}$  and 756 mm. N = 5.7.

$C_{12}H_{13}O_6N$  requires N = 5.3 per cent.

This oxime dissolves readily in hot water and, on cooling, separates as an oil.

*Semicarbazone of Brazilic Acid*,  $C_{13}H_{15}O_6N_3$ .—Brazilic acid appar-

ently combines with semicarbazide only with difficulty, as the following experiment shows. About 1 gram of the acid was dissolved in hot water and mixed with 1.5 grams of semicarbazide hydrochloride and 1.5 grams of sodium acetate and allowed to stand. After a few days, a thick oil had separated, which, on vigorous stirring, soon solidified to a mass of minute crystals; these appeared to consist of the semicarbazone mixed with small quantities of unchanged brazilic acid, since the substance contained only 11 per cent. of nitrogen, instead of 13.6 per cent. required by the formula  $C_{13}H_{15}O_6N_3$ . The filtrate from the crystals deposited, in the course of a few days, a hard, compact crust of crystals, which were collected, washed well, and dried at 100°. On analysis:

0.165 gave 18.4 c.c. nitrogen at 17° and 747 mm.  $N = 12.7$ .

$C_{13}H_{15}N_3O_6$  requires  $N = 13.6$  per cent.

The substance began to decompose at 125–126°, then at about 150–160° it became quite solid, and a few degrees higher it again decomposed and was converted into a black mass. That this substance, although not quite pure, is the semicarbazone of brazilic acid was proved by dissolving it in hot hydrochloric acid, when, on cooling, the solution became filled with needle-shaped crystals of pure brazilic acid.

#### *Lactone of Dihydrobrazilic Acid.*

Brazilic acid is readily reduced by sodium amalgam with formation of the sodium salt of dihydrobrazilic acid, and on acidifying this the  $\gamma$ -hydroxy-acid at once loses water with formation of its lactone.

The pure sodium salt of brazilic acid (0.5 gram) was dissolved in water, the solution placed in a flat, porcelain dish cooled by running water, and treated with 3 per cent. sodium amalgam (100 grams) in small quantities at a time. On acidifying the product, an oily substance separated which was at first partly soluble in sodium carbonate and therefore probably contained some hydroxy-acid. In order to convert the whole into the lactone, the strongly acid liquid was warmed for a few minutes on the water-bath.

After repeatedly extracting with pure ether, the solution was dried over calcium chloride and evaporated to a small bulk, when, on standing, small, colourless, glistening crystals separated: these were collected, washed with ether, and analysed.

0.1753 gave 0.3949  $CO_2$  and 0.0831  $H_2O$ .  $C = 61.4$ ;  $H = 5.3$ .

0.1052 „ 0.2354  $CO_2$  „ 0.0498  $H_2O$ .  $C = 61.0$ ;  $H = 5.2$ .

$C_{12}H_{12}O_5$  requires  $C = 61.0$ ;  $H = 5.1$  per cent.

The lactone of dihydrobrazilic acid melts at 142–144° and is sparingly soluble in dry ether; it dissolves readily in warm water and



separates on cooling as an oil which, however, soon crystallises ; it is readily soluble in alcohol, moderately so in chloroform and benzene, and sparingly soluble in light petroleum. When heated in small quantities in a test-tube, it decomposes to a large extent and gives an oily distillate smelling of coumarin ; this solidifies on rubbing, and on crystallising from water some of the lactone is recovered, showing that it distils to some extent without decomposition.

The lactone dissolves in baryta water, yielding a readily soluble barium salt, but is insoluble in cold sodium carbonate ; on boiling, however, it dissolves, and the solution, if well cooled and acidified, remains clear and evidently contains the hydroxy-acid, since, if heated to boiling and again cooled, the lactone separates. Concentrated sulphuric acid colours the crystals an intense crimson, and on standing a deep crimson solution is produced ; this, on warming, becomes at first more intensely coloured, and then the crimson changes to dark brown.

#### *Anhydrobrazilic Acid.*

This acid is obtained when brazilic acid is treated with sulphuric acid under the following conditions. Pure brazilic acid (0.3 gram) is dissolved in 5 c.c. of sulphuric acid and the test-tube containing the solution plunged into boiling water for  $1\frac{1}{2}$  to 2 minutes ; the dark brown solution is then cooled and mixed with 2 vols. of water when, on rubbing with a glass rod, a pale yellow, crystalline substance quickly separates. The sparingly soluble precipitate is collected on the pump, washed well, and dissolved in boiling water, a little purified animal charcoal being added, when, on cooling the filtered solution, a sandy, crystalline powder is deposited which consists of pure anhydro-brazilic acid.

In the preparation of this acid, it was found best to always work with the quantities given above ; if larger quantities are used, the yield obtained is not nearly so good. From the sulphuric acid mother liquors, small quantities of the anhydro-acid mixed with some unchanged brazilic acid may be extracted with ether and the two acids may then be separated by crystallisation from water.

The total yield of anhydrobrazilic acid obtained is, however, not more than 50 per cent. of the brazilic acid used, the loss being apparently due to some of the latter acid becoming sulphonated during the process of preparation. On analysis :

0.1635 gave 0.3681  $\text{CO}_2$  and 0.0645  $\text{H}_2\text{O}$ .  $\text{C} = 61.4$  ;  $\text{H} = 4.4$ .

0.1472 „ 0.3319  $\text{CO}_2$  „ 0.0580  $\text{H}_2\text{O}$ .  $\text{C} = 61.5$  ;  $\text{H} = 4.4$ .

$\text{C}_{13}\text{H}_{10}\text{O}_5$  requires  $\text{C} = 61.5$  ;  $\text{H} = 4.3$  per cent.

*Anhydrobrazilic acid* is very sparingly soluble in water and melts at  $197^\circ$ . When heated in a test-tube, it decomposes and gives a brown

oily distillate which, on cooling, solidifies and has an odour strongly resembling that of coumarin. It dissolves readily in alcohol, but is sparingly soluble in benzene, chloroform, or ether, and almost insoluble in light petroleum. It behaves like an unsaturated acid, since its solution in sodium carbonate rapidly decolorises permanganate. That it is a monobasic acid is shown by the results obtained by titrating it with decinormal sodium hydroxide.

0.1536 required for neutralisation 0.0264 NaOH, whereas this amount of a monobasic acid,  $C_{12}H_{10}O_5$ , should neutralise 0.0263 NaOH.

*Oxime of Anhydrobrazilic Acid*,  $C_{12}H_{11}NO_5$ .—In preparing this oxime, a small quantity of the acid was dissolved in sodium bicarbonate, mixed with an excess of a solution of hydroxylamine hydrochloride which had been neutralised with sodium carbonate, and the whole allowed to stand for 24 hours. On acidifying, the product deposited an oil, but this rapidly solidified to a granular precipitate, which was collected, washed well, and recrystallised from boiling water. It was thus obtained as a sandy powder consisting of microscopic needles, which melted with decomposition at about 175–180°. On analysis :

0.1533 gave 0.3260  $CO_2$  and 0.0629  $H_2O$ . C = 57.9 ; H = 4.5.

0.1567 „ 7.9 c.c. nitrogen at 20° and 760 mm. N = 5.8.

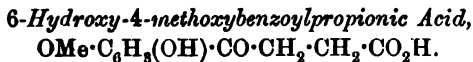
$C_{12}H_{11}NO_5$  requires C = 57.8 ; H = 4.4 ; N = 5.6 per cent.

*Oxidation of Anhydrobrazilic Acid. Formation of p-Methoxysalicylic Acid*,  $OMe \cdot C_6H_4(OH) \cdot CO_2H$ .—The pure acid (0.5 gram) was dissolved in dilute sodium carbonate and a cold saturated solution of permanganate added drop by drop with constant shaking until the pink colour remained permanent. After sufficient sodium sulphite had been added to destroy the excess of permanganate, the whole was boiled, filtered, and the filtrate and washings of the manganese precipitate evaporated to a small bulk. On acidifying, a colourless acid separated which crystallised from water in colourless needles. On analysis :

0.1104 gave 0.2299  $CO_2$  and 0.0495  $H_2O$ . C = 56.8 ; H = 4.9.

$C_8H_8O_4$  requires C = 57.1 ; H = 4.8 per cent.

This acid melted at 156°, and its aqueous solution gave, with ferric chloride, an intense violet coloration. That it was *p*-methoxysalicylic acid was further proved by mixing it with an equal quantity of this acid, when the mixture melted at 155–156°.



Anhydrobrazilic acid dissolves readily in warm barium hydroxide solution, and if the solution is boiled a thick, crystalline precipitate of the

barium salt of hydroxymethoxybenzoylpropionic acid rapidly forms, the separation being complete after 15 to 20 minutes.

If the solution is dilute, the separation does not take place until it is concentrated sufficiently, and then the barium salt separates in stellate groups. The barium salt is collected on the pump, washed with water, and dissolved in warm dilute hydrochloric acid, when, on standing, the free acid separates in colourless needles, and by recrystallisation from water is readily obtained pure, in long threads somewhat resembling crystals of sublimed phthalic acid. On analysis :

0.1714 gave 0.3702  $\text{CO}_2$  and 0.0840  $\text{H}_2\text{O}$ .  $\text{C} = 58.9$ ;  $\text{H} = 5.4$ .

0.1541 „ 0.3329  $\text{CO}_2$  „ 0.0756  $\text{H}_2\text{O}$ .  $\text{C} = 58.9$ ;  $\text{H} = 5.4$ .

$\text{C}_{11}\text{H}_{12}\text{O}_5$  requires  $\text{C} = 58.9$ ;  $\text{H} = 5.3$  per cent.

6-Hydroxy-4-methoxybenzoylpropionic acid melts at  $155-156^\circ$  and dissolves readily in hot, but is rather sparingly soluble in cold, water; its aqueous solution gives an intense violet coloration with ferric chloride.

The barium salt, obtained by the action of barium hydroxide on anhydrobrazilic acid in the way described above, after drying at  $100^\circ$ , was analysed with the following results :

0.3987 gave 0.2440  $\text{BaSO}_4$ .  $\text{Ba} = 36.1$ .

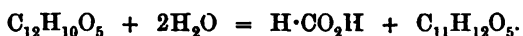
$\text{C}_{11}\text{H}_{10}\text{O}_5\text{Ba}, \text{H}_2\text{O}$  requires  $\text{Ba} = 36.4$  per cent.

From this it would appear that the barium salt prepared in this way has the formula  $\text{C}_{11}\text{H}_{10}\text{O}_5\text{Ba}, \text{H}_2\text{O}$ , that is to say, that the barium has replaced, not only the hydrogen of the carboxyl group, but also that of the phenolic hydroxyl group.

Such cases as this have often been observed before; thus salicylic acid yields a barium salt,  $\text{C}_7\text{H}_4\text{O}_3\text{Ba}, 2\text{H}_2\text{O}$ , which is very sparingly soluble in water.

The filtrates from several preparations of the barium salt of hydroxymethoxybenzoylpropionic acid were mixed and the excess of barium hydroxide removed by passing carbon dioxide through the boiling solution.

The filtrate deposited, on evaporation, a further small quantity of the insoluble barium salt; this was removed by filtration, and the concentrated solution, which contained a considerable quantity of a barium salt, carefully tested for formic acid. This was easily proved to be present, not only by the fact that the solution blackened silver nitrate, but also because it readily reduced mercuric chloride to mercurous chloride. There can, therefore, be no doubt that anhydrobrazilic acid is decomposed by boiling with barium hydroxide into formic acid and hydroxymethoxybenzoylpropionic acid, according to the equation



*Dimethoxybenzoylpropionic Acid*,  $C_6H_3(OMe)_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$ .

It was necessary to prepare this acid, in order to compare it with the acid obtained synthetically by the action of aluminium chloride on the mixture of dimethylresorcinol and the ester of the half-chloride of succinic acid (see next section).

Hydroxymethoxybenzoylpropionic acid (1 gram) was dissolved in 12 grams of methyl alcohol, 3 grams of concentrated sulphuric acid added, and the whole heated to boiling in a reflux apparatus for 4 hours.

On adding water, a crystalline substance separated, which, since it was insoluble in sodium carbonate, evidently consisted of the methyl ester,  $OMe \cdot C_6H_3(OH) \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2Me$ . In this condition, it melted at about  $85^\circ$ , and its alcoholic solution gave an intense violet with ferric chloride; it was, however, not further purified, owing to the necessity for using the whole quantity for further methylation. The dry methyl ester (0.8 gram) was dissolved in dilute sodium methoxide (containing 0.1 gram Na) and heated in a sealed tube with 3 grams of methyl iodide at  $120^\circ$  for 2 hours; the tube was then opened, the same quantity of sodium methoxide and methyl iodide again added, the tube resealed, and heated at  $120$ — $130^\circ$  for 3 hours. The product was poured into water, the oily precipitate extracted with ether, the ethereal solution well washed with water, and then three times with dilute soda in order to extract some unmethylated ester which was present. The ethereal solution was then evaporated and the residual oil hydrolysed by boiling for a few minutes with methyl alcoholic potash. Water was then added and the clear solution evaporated until free from methyl alcohol, when, on the addition of hydrochloric acid, a crystalline acid was deposited, which was collected, washed with water, dried on a porous tile, and recrystallised twice from benzene. On analysis:

0.1250 gave 0.2779  $CO_2$  and 0.0673  $H_2O$ .  $C = 60.6$ ;  $H = 6.0$ .

$C_{13}H_{14}O_5$  requires  $C = 60.5$ ;  $H = 5.9$  per cent.

*Dimethoxybenzoylpropionic acid* melts at  $146$ — $148^\circ$ , with slight previous softening, and when kept a short time a few degrees above its melting point, it becomes a deep violet colour. It is readily soluble in alcohol and in hot benzene, but sparingly so in cold benzene; its alcoholic solution gives no coloration with ferric chloride.

*Synthesis of Dimethoxybenzoylpropionic Acid.*

[With E. ORMEROD.]

In synthesising this acid, a process was employed which is somewhat similar to that recommended by L. Bouveault (*Bull. Soc. Chim.*, 1897, [iii], 17, 333) as suitable for cases of this kind.

Dimethylresorcinol (8.4 grams) was dissolved in nitrobenzene (17 grams) and carbon disulphide (35 grams), and then mixed with the ester of the half-chloride of succinic acid,  $\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  (10 grams). Powdered aluminium chloride\* (8 grams) was then added in small quantities and, after standing for some hours, the mixture was gently heated on the water-bath for a few minutes.

The product was treated with water, the oily layer well washed with water, and the carbon disulphide removed on the water-bath; the residue was then distilled in steam until the nitrobenzene and small quantities of unchanged dimethylresorcinol had been removed. The non-volatile oil was extracted with ether, the ethereal solution evaporated, and the brown oil hydrolysed with a slight excess of alcoholic potash. After evaporating off the alcohol, the residue was dissolved in water and acidified, when a brown solid separated, which was collected on the pump and purified by repeated recrystallisation from benzene. On analysis:

0.1559 gave 0.3465  $\text{CO}_2$  and 0.0834  $\text{H}_2\text{O}$ .  $\text{C} = 60.6$ ;  $\text{H} = 5.9$ .

$\text{C}_{12}\text{H}_{14}\text{O}_5$  requires  $\text{C} = 60.5$ ;  $\text{H} = 5.9$  per cent.

The synthetical dimethoxybenzoylpropionic acid thus obtained melted at  $146\text{--}148^\circ$  with slight previous softening, and the melted mass became a deep violet colour a few degrees above this temperature. That it is identical with the acid of this composition obtained from anhydrobrazilic acid as described above, was further proved by mixing the two acids, when no alteration in the melting point could be observed.

In conclusion, I wish to express my thanks to Mr. J. Yates for his valuable assistance in carrying out this investigation, and I wish also to state that much of the expense incurred was defrayed by repeated grants from the Royal Society Fund.

THE OWENS COLLEGE,  
MANCHESTER.

\* Prepared from aluminium.

XXIV.—*Brazilin and Hæmatoxylin. Part III. The Constitution of Hæmatoxylin.*

By W. H. PERKIN, jun., and J. YATES.

HÆMATOXYLIN is the colouring matter of *Hæmatoxylon campechianum*, a tree which belongs to the family *Cæsalpiniaceæ*, and the wood of which appears to have been first imported into Europe by the Spaniards shortly after the discovery of America. The heart-wood of this tree, known as logwood in this country, is still largely used in cotton and wool dyeing for the production of blacks and greys, and it is also employed on account of its cheapness along with other colours, such as indigo, for dyeing compound shades.

The importance of hæmatoxylin may be judged from the fact that it has probably been, and perhaps is still, more largely used than any other natural colouring matter, not even excepting indigo. The dye is sent into the market either as a concentrated liquid extract or in the solid form, the rasped wood, in either case, being extracted with water and the extract evaporated in vacuum pans.

For dyeing cotton, or in calico printing, logwood extract is generally used in conjunction with an iron, chromium, or aluminium mordant; the two first-named give intense black, whereas, with the latter, greyish-violet shades are produced. Very large quantities of the liquid extract are still used in wool dyeing for the production of blacks, the wool being immersed alternately in the extract, and in a bath of potassium dichromate and sulphuric acid. Again, in silk dyeing, logwood extract is very largely used in conjunction with an iron mordant for the production of blacks. It is worthy of note that hæmatoxylin and iron alum have long been used as one of the most important stains for microscopical sections of animal tissues, but, quite recently, Professor S. J. Hickson (*Quart. J. Micros. Sci.*, 1901, p. 469) has shown that brazilin used with iron alum gives results which are even more satisfactory.

The actual colouring matter of logwood was first isolated by Chevreul (*Ann. Chim. Phys.*, [ii], 82, 53, 126) in 1810, who obtained it by extracting the wood with water, evaporating the extract to dryness, and digesting the residue with alcohol, which dissolved the hæmatoxylin, but not the other substances present.

After distilling off the alcohol, the residue was allowed to stand in contact with water, when the hæmatoxylin separated in crystals. Pure hæmatoxylin is now comparatively easily obtained from the dark coloured crusts which gradually separate when the casks of concentrated logwood extract are allowed to stand in a cool place. The crude mass

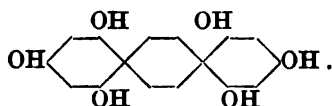
is ground to a fine powder, extracted repeatedly with ether, the ethereal solution evaporated, and the residue left in contact with water when dark coloured crystals separate, which, by recrystallisation from water containing a small quantity of sodium bisulphite, may be obtained colourless, and consist then of pure hæmatoxylin.

Hæmatoxylin crystallises in tetragonal prisms with 3 molecules of water of crystallisation, and is sparingly soluble in cold, but readily in hot, water; it dissolves in alkalis, forming an intense purple-coloured solution. It is strongly dextrorotatory, a 1 per cent. aqueous solution having a rotation of  $1.85^\circ$  in a 200 mm. tube; it also reduces Fehling's solution and silver nitrate in the cold.

The first attempt to determine the composition of hæmatoxylin is due to Erdmann, who in 1842 (*Annalen*, 44, 292) proposed the formula  $C_{40}H_{17}O_6$ ; this he subsequently altered to  $C_{16}H_{14}O_6$ , for the anhydrous substance and this formula, which was confirmed by Hesse (*Annalen*, 1859, 109, 332) and by other workers, is now accepted as correct.

From very early times experiments were made with the object of obtaining evidence as to the nature of this important dye-stuff, but the results in most cases did not afford any clue to its constitution. The literature bearing on the subject is, in fact, so extended, that it is only possible in this paper to give a very brief outline of such of the work as produced really valuable evidence of the nature of hæmatoxylin.

Reim (*Ber.*, 1871, 4, 331) showed that when an ethereal solution of hæmatoxylin is mixed with a few drops of nitric acid, oxidation takes place and hæmatein,  $C_{16}H_{12}O_6$ , is produced. J. J. Hummel and A. G. Perkin (*Ber.*, 1882, 15, 2337) subsequently obtained hæmatein pure in the form of reddish-brown crystals by leading air through a solution of the dye-stuff in ammonia. The action of fused caustic potash on hæmatoxylin was also first investigated by Reim (*loc. cit.*, 332) and from the fused mass he was able to isolate considerable quantities of *pyrogallol*, a result of great importance, since it showed that hæmatoxylin is probably a derivative of this substance. R. Meyer (*Ber.*, 1879, 12, 1392) submitted hæmatoxylin to dry distillation, and obtained a distillate which he stated contained resorcinol, as well as *pyrogallol*, but the qualitative tests by which he claimed to have recognised the former of these were quite insufficient, and it will be shown in this paper that resorcinol is not formed in this way. That hæmatoxylin contains several hydroxyl groups was clear from early times, and in order to determine how many such groups were present in the molecule, Reim (*loc. cit.*, 331) investigated its behaviour with acetyl chloride, and obtained a substance which he considered to be hexa-acetyl hæmatoxylin,  $C_{16}H_8O_6(C_2H_3O)_6$ , and as a result of this he suggested the first constitutional formula for hæmatoxylin, namely,



Erdmann and Schultz (*Annalen*, 1883, 216, 234), by determining the number of acetyl groups in this substance, subsequently showed that Reim's substance was *penta-acetylhæmatoxylin* and had the formula  $C_{16}H_9(C_2H_3O)_5O_6$ , and therefore hæmatoxylin contains only five hydroxyl groups. This result was confirmed by the investigation of the action of sodium methoxide and methyl iodide on hæmatoxylin when, under certain conditions (Herzig, *Monatsh.*, 1894, 15, 143), tetramethylhæmatoxylin,  $C_{16}H_{10}O_2(OMe)_4$ , is produced a substance which still contains a hydroxyl group, since on treatment with acetic anhydride it yields acetyl tetramethylhæmatoxylin,



It is thus shown that hæmatoxylin, like brazilin, contains an alcoholic hydroxyl group which is not methylated by the action of sodium methoxide and methyl iodide, and indeed, from the general similarity between brazilin and hæmatoxylin, it has long been considered probable that these two colouring matters are closely allied in constitution.

During the investigation of brazilin, we have also carried out a number of experiments on hæmatoxylin, the results of which, in our opinion, not only prove the close relationship of these two colouring matters, but also enable us to assign a formula to hæmatoxylin which we believe correctly represents the constitution of this substance.

In the present paper, we describe only the experiments on the oxidation of tetramethylhæmatoxylin with permanganate, and leave for a future communication the description of the interesting substances which have been obtained by oxidising tetramethylhæmatoxylin with chromic acid.

We have also carefully repeated R. Meyer's (*loc. cit.*) experiments on the distillation of hæmatoxylin, and show that pyrogallol (but no resorcinol) is produced in considerable quantity in this way. We are thus able to confirm Reims' discovery (*loc. cit.*) that hæmatoxylin is probably a derivative of pyrogallol.

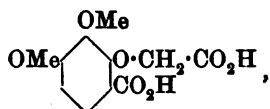
When tetramethylhæmatoxylin is oxidised with permanganate, it yields *m-hemipinic acid*, an important result, because it shows that hæmatoxylin, like brazilin, contains the catechol nucleus. Briefly stated, then, the molecule of brazilin is made up of a resorcinol and a catechol nucleus, whereas hæmatoxylin contains a pyrogallol and a catechol nucleus.

From the product of the oxidation of tetramethylhæmatoxylin, we

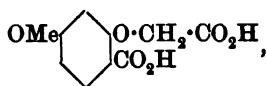


have also been able to isolate considerable quantities of a beautifully crystalline acid,  $C_{11}H_{12}O_7$ , which melts at  $215^\circ$ .

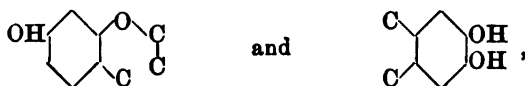
This acid is dibasic, since it yields a silver salt,  $C_{11}H_{10}O_7Ag_2$ ; it is also converted into the anhydride  $C_{11}H_{10}O_6$  by treatment with acetic anhydride, and as it contains two methoxy-groups and yields pyrogallol when heated in a sealed tube with hydrochloric acid, its constitution is evidently represented by the formula :



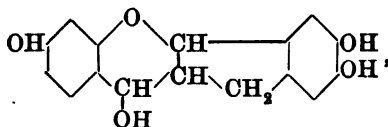
that is to say, it is *2-carboxy-5 : 6-dimethoxyphenoxyacetic acid*. This acid is therefore exactly similar to the *2-carboxy-5-methoxyphenoxyacetic acid* :



which was obtained from trimethylbrazilin by oxidation with permanganate, from which, indeed, it only differs by containing an extra methoxy-group. The close relationship between brazilin and hæmatoxylin which owing to the general similarity in the properties of these two colouring matters has so long been considered probable, is now clearly proved and may be briefly expressed in the following way. Trimethylbrazilin, on oxidation, yields 2-carboxy-5-methoxyphenoxyacetic acid and *m*-hemipinic acid, and therefore its constitutional formula must contain the two nuclei :

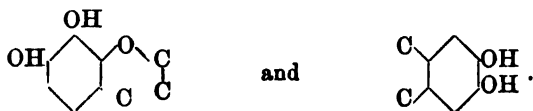


These two combined together lead, then, to the formula,

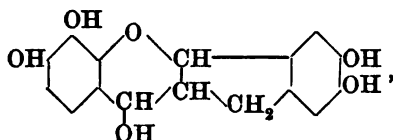


which, as shown in the preceding paper, there is every reason to believe represents the constitution of brazilin.

Similarly, tetramethylhæmatoxylin, on oxidation with permanganate, yields 2-carboxy-5 : 6-dimethoxyphenoxyacetic acid and *m*-hemipinic acid, and therefore hæmatoxylin must contain the two nuclei :



These combined together in the same way as in the construction of the brazilin formula give the expression

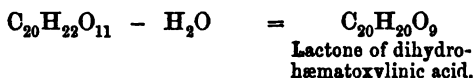
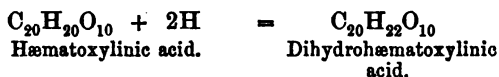


as representing the constitution of hæmatoxylin, and as this accounts in a satisfactory manner for all the known decompositions of this colouring matter, there can be little doubt that it is correct.

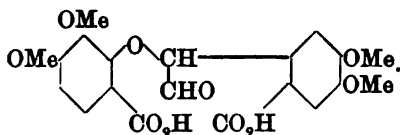
Besides the acids mentioned above, another acid is formed in the oxidation of tetramethylhæmatoxylin with permanganate in considerable quantities; this melts at 180°, has the formula  $C_{20}H_{20}O_{10}$ , and has been named *hæmatoxylinic acid*.

This new acid, which it will be seen contains the same number of carbon atoms as tetramethylhæmatoxylin, is dibasic, since its silver salt has the composition  $C_{20}H_{18}Ag_2O_{10}$ .

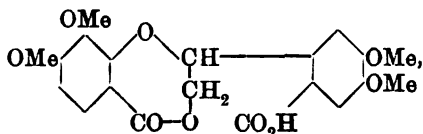
On reduction with sodium amalgam, it is converted quantitatively into an acid,  $C_{20}H_{20}O_9$ , which is a monobasic lactonic acid, and it is therefore evident that the latter is produced in two stages, thus:



Hæmatoxylinic acid corresponds in all its properties with brazilinic acid,  $C_{19}H_{18}O_9$  (Trans., 1901, 79, 1411), from which it differs only by one methoxy-group, and it is extremely probable that its constitution is:



The lactone of dihydrohæmatoxylinic acid would then be



or the  $CO_2H$  of the catechol nucleus might of course take part in the

lactone formation. To prove conclusively the constitutions of brazilinic and hæmatoxylinic acids is a matter of great difficulty, and a description of the large amount of experimental work which has been accumulated with this object will, it is hoped, form the subject matter of a future communication.

*Oxidation of Tetramethylhæmatoxylin\* with Permanganate.*

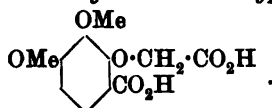
This oxidation, like the oxidation of trimethylbrazilin, was carried out under a variety of conditions, but the following method was the one ultimately adopted in preparing the substances described in this paper.

Tetramethylhæmatoxylin (10 grams) is ground up with a little water into the finest possible paste, washed into a three litre flask with 100 c.c. of water, and then 100 c.c. of a cold saturated solution of permanganate added and the whole allowed to stand at the ordinary temperature until the colour has disappeared. A further 100 c.c. of permanganate are then added, and the operation continued until, after standing for 10—12 hours, the liquid still remains pink. The excess of permanganate is then destroyed by adding sodium sulphite and the product, after heating to boiling, filtered on the pump; the manganese precipitate is then extracted twice with boiling water and the combined aqueous solutions nearly neutralised with hydrochloric acid and evaporated to a small bulk, but not to dryness.

On acidifying the residue with hydrochloric acid, a small quantity of a black, tarry substance separates and is removed by filtration, the red filtrate is then shaken with chloroform, which causes a small quantity of a crystalline substance (A) to separate; the filtrate from this is then repeatedly extracted with chloroform. The chloroform extract is washed with a little water, dried over calcium chloride, when, on distilling off the chloroform, a semi-solid tarry mass remains (B). The solution, after treatment with chloroform, is saturated with ammonium sulphate and extracted at least 10 times with ether; the ethereal solution is dried over calcium chloride and evaporated and in this way a brick-red, crystalline mass is obtained (C).

\* The hæmatoxylin used in this research was obtained from Kahlbaum and was always of excellent quality. The preparation of the tetramethylhæmatoxylin was carried out almost exactly in the way described in the case of trimethylbrazilin (Trans., 1901, 79, 1403). On pouring the product of methylation into water and allowing the whole to stand for a few days, in almost all cases, part of the tetramethylhæmatoxylin separated in roseate groups of straw-coloured needles; these melted at 65—70° and contained water of crystallisation. After drying at 100° and recrystallising from alcohol, the substance was obtained in an anhydrous condition melting at 140—142°. The rest of the tetramethylhæmatoxylin was extracted with ether and purified as in the case of the trimethylbrazilin: but in the oxidation experiments, much better results were always obtained with the crystals melting at 65—70° than with the anhydrous substance.

*The Substance A is 2-Carboxy-5:6-dimethoxyphenoxyacetic Acid,*



The substance A crystallises from glacial acetic acid in colourless needles and so easily that even when much contaminated with resin, as was frequently the case, it separates at once from this solvent in an almost pure condition. After two crystallisations, the following numbers were obtained on analysis :

0.1730 gave 0.3258  $\text{CO}_2$  and 0.0753  $\text{H}_2\text{O}$ . C = 51.4 ; H = 4.8.

0.1153 „ 0.2179  $\text{CO}_2$  „ 0.0495  $\text{H}_2\text{O}$ . C = 51.5 ; H = 4.8.

$\text{C}_{11}\text{H}_{12}\text{O}_7$  requires C = 51.6 ; H = 4.7 per cent.

*2-Carboxy-5:6-dimethoxyphenoxyacetic acid* melts at  $214\text{--}215^\circ$  and at about  $225\text{--}230^\circ$  decomposes with evolution of gas. It is almost insoluble in cold water, but is dissolved slightly by boiling water and is deposited on cooling in needles ; it is sparingly soluble in cold acetic acid, but dissolves readily on boiling.

The methoxy-groups were determined by Zeisel's method :

0.2703 gave 0.5148  $\text{AgI}$ .  $\text{MeO} = 25.2$ .

$\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_2(\text{MeO})_2\text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  requires  $\text{MeO} = 24.2$  per cent.

*The silver salt*,  $\text{C}_{11}\text{H}_{10}\text{O}_7\text{Ag}_2$ , is precipitated on the addition of silver nitrate to a neutral solution of the ammonium salt as a white, gelatinous precipitate which is difficult to wash. On analysis :

0.2251 gave 0.2343  $\text{CO}_2$ , 0.0457  $\text{H}_2\text{O}$ , and 0.1035  $\text{Ag}$ . C = 28.3 ; H = 2.2 ;  
Ag = 46.0.

$\text{C}_{11}\text{H}_{10}\text{O}_7\text{Ag}_2$  requires C = 28.1 ; H = 2.1 ; Ag = 45.9 per cent.

A neutral solution of the ammonium salt gives a white, gelatinous precipitate with calcium chloride, but with barium chloride no precipitate is produced until the solution is boiled, and then a very sparingly soluble, crystalline salt separates. When fused with potash, the acid gives a brown mass, and the solid acid obtained from this by acidifying and extracting with ether gives all the reactions of pyrogallol.

In order to clearly prove that this acid is a derivative of pyrogallol, a small quantity was heated with hydrochloric acid in a sealed tube for 2 hours at  $180^\circ$ . On opening the tube, carbon dioxide escaped, and the liquid contained small, black flocks in suspension ; these were removed by filtration. The filtrate was saturated with ammonium sulphate, extracted five times with ether, and the ethereal solution, after drying with calcium chloride, evaporated, when a brown oil remained

which was distilled under reduced pressure from a small retort. The distillate, which was a light brown oil, crystallised at once on rubbing with a trace of pyrogallol, and, in contact with porous porcelain, the dark mother liquor was rapidly absorbed, leaving a colourless, crystalline residue. After crystallising from benzene, this melted at  $125-130^{\circ}$ , gave with ferric chloride a blue colour rapidly changing to brownish-green, and with nitrous acid a yellow colour changing to brown, and since when dissolved in potash and left exposed to air a deep brown solution was obtained, there can be no doubt that the substance is pyrogallol (m. p.  $132^{\circ}$ ).

*Anhydride of Carboxydimethoxyphenoxyacetic Acid.*

When this acid is heated in a small flask under reduced pressure, it first melts, then water is eliminated, and an oily distillate is obtained which has a penetrating odour like that of formaldehyde, and which, on cooling and rubbing, partly solidifies. When this was ground up with ether, some dissolved, but a portion remained insoluble as a white, crystalline powder which softened at  $150^{\circ}$  and melted at  $175^{\circ}$ . This substance dissolved only partly in cold dilute sodium carbonate, and the solution, on acidifying, deposited a considerable quantity of the unchanged acid melting at  $214^{\circ}$ . The residue consisted of the crude anhydride of the acid.

It appears, therefore, that on distillation under reduced pressure the acid is partly converted into the anhydride and partly distils unchanged.

Subsequently, the pure anhydride was obtained by heating the acid in a reflux apparatus with acetic anhydride for 20 minutes. The solution, on standing over potash in a vacuum desiccator, gradually deposited square plates from which, after drying at  $100^{\circ}$ , the following numbers were obtained on analysis :

0.1488 g. gave 0.3013  $\text{CO}_2$  and 0.0575  $\text{H}_2\text{O}$ .  $\text{C} = 55.2$  ;  $\text{H} = 4.3$ .

$\text{C}_{11}\text{H}_{10}\text{O}_6$  requires  $\text{C} = 55.4$  ;  $\text{H} = 4.2$  per cent.

This substance is therefore the *anhydride of carboxydimethoxyphenoxyacetic acid*.



The substance C, obtained from the ethereal extract (p. 240) of the product of the oxidation of trimethylhæmatoxylin with permanganate, was a brick-red powder sparingly soluble in ether. In purifying it, it was first washed on the pump with ether and then crystallised from water with the aid of animal charcoal, and was thus obtained in almost

colourless, glistening needles which melted at  $190^{\circ}$  with decomposition and consisted of pure *m*-hemipinic acid. On analysis :

0.1284 gave 0.2496  $\text{CO}_2$  and 0.0529  $\text{H}_2\text{O}$ .  $\text{C} = 53.0$  ;  $\text{H} = 4.6$ .

$\text{C}_{10}\text{H}_{10}\text{O}_6$  requires  $\text{C} = 53.1$  ;  $\text{H} = 4.4$  per cent.

As it was most important to be certain of the identity of this acid, it was next converted into the silver salt, which was obtained as a granular precipitate on adding silver nitrate to a neutral solution of the ammonium salt. On analysis :

0.1489 gave 0.1517  $\text{CO}_2$ , 0.0279  $\text{H}_2\text{O}$ , and 0.0728 Ag.  $\text{C} = 27.7$  ;  
 $\text{H} = 2.1$  ;  $\text{Ag} = 48.8$ .

$\text{C}_{10}\text{H}_8\text{O}_6\text{Ag}_2$  requires  $\text{C} = 27.3$  ;  $\text{H} = 1.9$  ;  $\text{Ag} = 49.1$  per cent.

Lastly, the characteristic ethylimide was prepared by dissolving the acid in ethylamine, evaporating to dryness, distilling the residue, and crystallising the distillate from alcohol. The yellow needles which separated melted at  $230^{\circ}$  and consisted of pure *m*-hemipinethylimide. On analysis :

0.1829 gave 9.6 c.c. of nitrogen at  $13^{\circ}$  and 732 mm.  $\text{N} = 6.2$ .

$\text{C}_{12}\text{H}_{13}\text{O}_4\text{N}$  requires  $\text{N} = 5.9$  per cent.

There can therefore be no doubt that the acid is *m*-hemipinic acid, a very important fact, since it proves that hæmatoxylin contains the catechol nucleus.

#### *Hæmatoxylinic Acid, $\text{C}_{20}\text{H}_{20}\text{O}_{10}$*

This acid is contained in the chloroform extract (B) of the product of the oxidation of tetramethylhæmatoxylin, and is evidently that derivative of hæmatoxylin which corresponds with brazilinic acid (Trans., 1901, 79, 1411) obtained in a similar way from trimethylbrazilin. The tarry residue left after distilling off the chloroform was boiled with a large quantity of water, when all dissolved except a small quantity of dark coloured, resinous matter. The aqueous solution was mixed with an excess of basic lead acetate, and the pale yellow, amorphous precipitate which separated was collected and well washed with water. The precipitate was then ground up with water to a fine paste and decomposed with sulphuretted hydrogen, first by passing the gas in the cold, and afterwards through the boiling liquid. After filtering, the precipitate was again heated with water and sulphuretted hydrogen, and the combined, nearly colourless filtrates were then evaporated to a small bulk. The concentrated aqueous solution, on standing, deposited nodular crystals ; these were collected, washed with water, and recrystallised from glacial acetic

acid, from which the new acid separated in colourless needles. On analysis :

0.1717 gave 0.3582  $\text{CO}_2$  and 0.0714  $\text{H}_2\text{O}$ .  $\text{C}=56.9$ ;  $\text{H}=4.6$ .

0.1546 „ 0.3231  $\text{CO}_2$  „ 0.0677  $\text{H}_2\text{O}$ .  $\text{C}=57.0$ ;  $\text{H}=4.8$ .

$\text{C}_{20}\text{H}_{20}\text{O}_{10}$  requires  $\text{C}=57.1$ ;  $\text{H}=4.8$  per cent.

*Hæmatoxylinic acid* melts at  $180^\circ$  without decomposition, and is very sparingly soluble in water; it dissolves readily in hot methyl alcohol and glacial acetic acid, but is sparingly soluble in chloroform, very sparingly so in benzene, and almost insoluble in light petroleum.

Hæmatoxylinic acid, like brazilinic acid, dissolves in concentrated sulphuric acid, producing an intense reddish-brown solution. That it is a dibasic acid is shown by the following results, obtained by titrating with decinormal sodium hydroxide.

0.2067 neutralised 0.041 gram  $\text{NaOH}$ , whereas this amount of a dibasic acid of the formula  $\text{C}_{20}\text{H}_{20}\text{O}_{10}$  should neutralise 0.04 gram  $\text{NaOH}$ .

*Salts of Hæmatoxylinic Acid.*—The silver salt,  $\text{C}_{20}\text{H}_{18}\text{O}_{10}\text{Ag}_2$ , is obtained as a white, granular precipitate on adding silver nitrate to a neutral solution of the ammonium salt. On analysis :

0.2201 gave 0.3030  $\text{CO}_2$ , 0.0549  $\text{H}_2\text{O}$ , and 0.0704  $\text{Ag}$ .  $\text{C}=37.6$ ;  $\text{H}=2.8$ ;  $\text{Ag}=33.6$ .

$\text{C}_{20}\text{H}_{18}\text{O}_{10}\text{Ag}_2$  requires  $\text{C}=37.8$ ;  $\text{H}=2.8$ ;  $\text{Ag}=34.0$  per cent.

The neutral solution of the ammonium salt gives no precipitate with calcium chloride, barium chloride, or zinc sulphate, but on the addition of copper sulphate a pale green, very sparingly soluble salt separates.

#### *Lactone of Dihydrohæmatoxylinic Acid, $\text{C}_{20}\text{H}_{20}\text{O}_9$ .*

This lactone acid is formed by the action of sodium amalgam on hæmatoxylinic acid, reduction and elimination of water taking place simultaneously, as explained in the introduction (p. 239).

In preparing the lactone acid, pure hæmatoxylinic acid was dissolved in dilute caustic soda and left in contact with excess of 3 per cent. sodium amalgam for 24 hours. On acidifying the strongly alkaline solution, a gelatinous precipitate separated, which was collected on the pump, washed with water, and purified by recrystallisation from glacial acetic acid, from which it separated in beautiful, colourless needles. On analysis :

0.1748 gave 0.377  $\text{CO}_2$  and 0.0759  $\text{H}_2\text{O}$ .  $\text{C}=58.8$ ;  $\text{H}=4.8$ .

0.1380 „ 0.2996  $\text{CO}_2$  „ 0.0621  $\text{H}_2\text{O}$ .  $\text{C}=59.2$ ;  $\text{H}=4.9$ .

$\text{C}_{20}\text{H}_{20}\text{O}_9$  requires  $\text{C}=59.4$ ;  $\text{H}=4.9$  per cent.

The lactone of dihydrohæmatoxylinic acid melts at  $192\text{--}193^\circ$  without decomposition, and is practically insoluble in cold water; it dis-

solves, however, slightly in boiling water, and the solution, on cooling, deposits the acid in the form of peculiar gelatinous flocks. It is moderately readily soluble in hot methyl alcohol, and separates on cooling in microscopic needles resembling asbestos threads; it is readily soluble in hot glacial acetic acid, but almost insoluble in chloroform, benzene, and light petroleum. Concentrated sulphuric acid colours the crystals a salmon-pink,\* and on standing a pink solution is formed, the colour of which becomes more intense on warming, and the solution on diluting with water deposits a white, amorphous precipitate.

That this new acid is a lactonic acid is shown by the following titration experiments:

I. 0.229 gram of substance, titrated with decinormal sodium hydroxide in the cold, neutralised 0.0234 gram NaOH, whereas this amount of a *monobasic* acid,  $C_{20}H_{20}O_9$ , should neutralise 0.0227 gram NaOH.

II. 0.2357 gram was boiled with excess of decinormal sodium hydroxide for 10 minutes and the excess determined by titration with decinormal sulphuric acid. It was found that 0.0478 gram NaOH had been neutralised, whereas, on the assumption that the lactone ring had been hydrolysed and the acid become *dibasic*, the amount of substance taken should have neutralised 0.0467 gram NaOH.

*Salts of the Lactone of Dihydrohæmatoxylinic Acid.*—The silver salt,  $C_{20}H_{19}O_9Ag$ , was prepared by adding silver nitrate to a neutral solution of the ammonium salt. It is a white, amorphous precipitate very sparingly soluble in water. On analysis:

0.1640 gave 0.2789  $CO_2$ , 0.0557  $H_2O$ , and 0.0342 Ag.  $C = 46.4$   
 $H = 3.8$ ;  $Ag = 20.9$ .

$C_{20}H_{19}O_9Ag$  requires  $C = 46.9$ ;  $H = 3.7$ ;  $Ag = 21.1$  per cent.

The neutral solution of the ammonium salt gives no precipitate with barium or calcium chlorides, even on boiling; copper sulphate gives a pale blue, very insoluble precipitate, and zinc sulphate a white, caseous salt which melts in boiling water.

### *Distillation of Hæmatoxylin.*

[With A. W. GILBODY.]

It was pointed out in the introduction (p. 237) that our results showed that hæmatoxylin must contain a pyrogallol and a catechol nucleus, and that the statement of R. Meyer (*Ber.*, 1889, 12, 1392), that this substance, on distillation, yields pyrogallol and *resorcinol*, was

\* This colour reaction is much less intense than that shown in the case of the corresponding lactone of dihydrobrazilinic acid, a substance which will be described in a future communication.



not in harmony with our work, and we therefore felt it necessary to repeat his experiments. In doing this, hæmatoxylin (10 grams) was distilled from a small retort under reduced pressure, and the brown, semi-solid distillate from ten such experiments was dissolved in water and filtered from a small quantity of insoluble resinous matter. The solution, which reacted strongly acid, was precipitated with excess of lead acetate and the voluminous lead salt, after washing with water, suspended in water and decomposed by sulphuretted hydrogen. The filtrate from the lead sulphide deposited, on evaporation, a brown, semi-solid mass, which was repeatedly extracted with hot benzene, when, on concentrating the benzene solution and allowing it to stand, a mass of crystals of nearly pure pyrogallol separated. After recrystallising from toluene with the aid of animal charcoal, the following results were obtained on analysis :

0.2046 gave 0.4274  $\text{CO}_2$  and 0.0878  $\text{H}_2\text{O}$ .  $\text{C} = 57.0$  ;  $\text{H} = 4.8$ .

$\text{C}_6\text{H}_3(\text{OH})_3$  requires  $\text{C} = 57.1$  :  $\text{H} = 4.8$  per cent.

The substance melted at  $130-131^\circ$  and showed all the reactions of pyrogallol. The filtrate from the lead salt, which should contain any resorcinol which had been formed, was acidified with sulphuric acid and extracted five times with ether. The ethereal solution was washed with dilute sodium hydrogen carbonate, dried over calcium chloride, and evaporated, when only a small quantity of a dark-coloured oil remained, which was found to contain traces of pyrogallol which had escaped precipitation by the lead acetate. We were not able, in spite of every careful experiments, to detect even a trace of resorcinol in this oil, and therefore conclude that the statement that resorcinol is formed by the distillation of hæmatoxylin is incorrect.

We wish to state that much of the expense which was incurred during this long investigation has been met by repeated grants from the Government Grant Fund of the Royal Society.

THE OWENS COLLEGE,  
MANCHESTER.

## XXV.—On *aa*-Dimethylglutaconic Acid and the Synthesis of isoCamphoronic Acid.

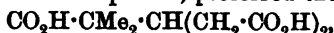
By W. H. PERKIN, jun.

isoCAMPBORONIC acid,  $\text{C}_9\text{H}_{14}\text{O}_6$ , has been obtained by the oxidation of campholenic acid, camphoroxime, and other derivatives of camphor, and it is also one of the products of the oxidation of pinene. For these

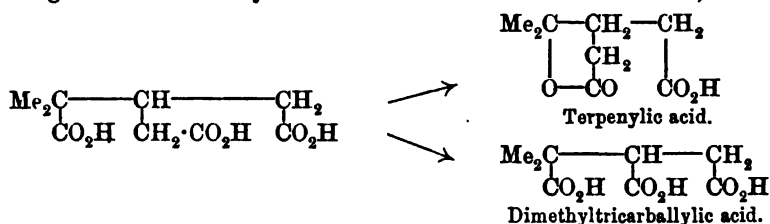
reasons the determination of the constitution of this acid has always been considered to be a matter of great importance, since, until this is definitely proved, it is not possible to obtain a correct view of the relationship which undoubtedly exists between the various members of the camphor and terpene series. For a considerable time, two views as to the constitution of *isocamphoronic acid* have been especially prominent. Baeyer (*Ber.*, 1896, 29, 2775), as the result of his classical researches on pinene, came to the conclusion that this acid probably had the constitution



whereas Tiemann (*ibid.*, 2612), who prepared the acid from campholenic acid as well as from pinene, preferred the formula



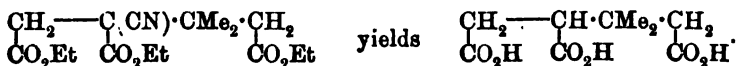
on account of the fact that *isocamphoronic acid*, when treated with concentrated sulphuric acid, is converted into *terpenylic acid*, and when oxidised with permanganate yields *dimethyltricarballic acid*, two changes which are easily understood with the aid of his formula,



but which are difficult to bring in agreement with Baeyer's formula.

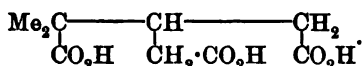
In order to decide whether either of these two formulæ represented *isocamphoronic acid*, an experimental investigation on the synthesis of the acids represented by these formulæ has been in progress during the last four years, and in a paper published some time since (Perkin and Thorpe, *Trans.*, 1899, 75, 897) a method was described by which it was found possible to synthesise the acid having the formula which Baeyer assigned to *isocamphoronic acid*. Briefly stated, this synthesis is as follows:

Ethyl dimethylacrylate,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , is heated with the sodium compound of ethylic cyanoacetate,  $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ , when condensation takes place and the sodium compound of ethyl cyanodimethylglutarate,  $\text{CO}_2\text{Et}\cdot\text{C}(\text{CN})\text{Na}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , is obtained. When this is heated with ethyl bromoacetate, ethyl cyanodimethylbutanetricarboxylate is produced, and this, on hydrolysis with hydrochloric acid, yields the dimethylbutanetricarboxylic acid, which is the acid represented by Baeyer's *isocamphoronic acid* formula,

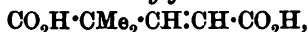


The acid thus obtained did not crystallise, and differed from *isocamphoronic* acid in many of its other properties, and it was therefore clearly proved that the latter cannot be a dimethylbutanetricarboxylic acid of this formula. Since these results were obtained, a great number of experiments have been carried out with the object of synthesising the acid having the formula which Tiemann considered must represent *isocamphoronic* acid, but until lately without success.

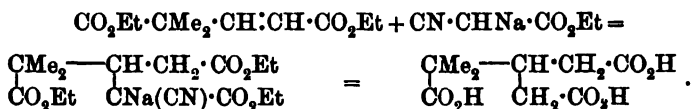
In the present paper, however, a method is described by which the acid of this formula has been synthesised, and it is shown that the synthetical acid is identical with *isocamphoronic* acid, and therefore Tiemann's view is the correct one, and *isocamphoronic* acid is



The synthesis of *isocamphoronic* acid may be briefly described as follows. *aa*-Dimethylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is converted into its anhydride, this is then brominated by treating it with phosphorus pentachloride and bromine, and the product poured into alcohol, when *ethyl a<sub>1</sub>-bromo-aa-dimethylglutarate* is obtained as an oil boiling at 170° (35 mm.). When this ester is digested with alcoholic potash, decomposition takes place readily, and one of the substances formed is a new *dimethylglutaconic acid*,



which melts at 172°. If, now, the ester of this acid is digested in alcoholic solution with the sodium compound of cyanoacetic ester, a condensation product is formed which, on hydrolysis with sulphuric acid, yields *isocamphoronic* acid. These changes may be represented thus:

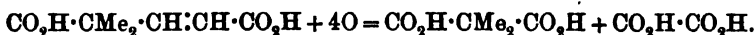


The acid thus obtained melted at the same temperature as *isocamphoronic* acid, and furthermore a mixture of equal parts of the synthetical acid and of *isocamphoronic* acid from pinene (which Professor von Baeyer kindly sent the author) melted at exactly the same temperature as the constituents. Finally, the synthetical acid, when heated with sulphuric acid, is converted into terpenylic acid with evolution of carbon monoxide, a reaction which, as Tiemann first showed, is highly characteristic of *isocamphoronic* acid. There can therefore be no doubt that the synthetical acid is the same as the *isocamphoronic* acid obtained from camphor and from pinene.

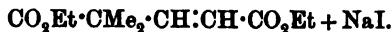
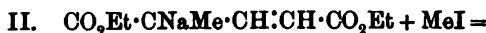
The *aa*-dimethylglutaconic acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , which

is formed from ethyl  $\alpha_1$ -bromo- $\alpha\alpha$ -dimethylglutarate by the action of alcoholic potash as described above, is an acid of considerable interest, for the following reasons:

It melts at  $172^\circ$  and is undoubtedly  $\alpha\alpha$ -dimethylglutaconic acid, since, on oxidation with permanganate, it is quantitatively converted into dimethylmalonic acid and oxalic acid:



Two other  $\alpha\alpha$ -dimethylglutaconic acids have, however, been described, namely, an acid melting at about  $133^\circ$ , which Henrich (*Monatsh.*, 1899, 20, 559) obtained by heating the sodium compound of glutaconic ester with methyl iodide and then again with sodium and methyl iodide and hydrolysing the product.

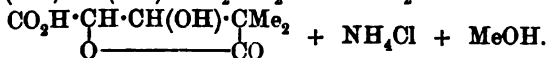
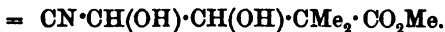


That this acid melting at about  $133^\circ$  is  $\alpha\alpha$ -dimethylglutaconic acid is proved by the fact that, on oxidation with permanganate, it also yields dimethylmalonic acid.

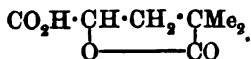
Conrad (*Ber.*, 1899, 32, 137; 1900, 33, 1921) has prepared a different acid melting at  $150^\circ$ , which he considers to be an  $\alpha\alpha$ -dimethylglutaconic acid, the process he employed being briefly as follows. Methyl bromodimethylacetoacetate was treated with potassium cyanide and thus converted into methyl cyanodimethylacetoacetate; this, on hydrolysis with acids or alkalis, yields a crystalline substance melting at  $214^\circ$ , which he considers to be the lactone of  $\alpha_1\beta$ -dihydroxy- $\alpha\alpha$ -dimethylglutaric acid. He thinks it probable that the formation of this substance takes place thus:



Methyl cyanodimethylacetoacetate.



By heating the lactone with hydriodic acid, he obtained a crystalline lactone melting at  $153^\circ$ , which he concludes is the lactone of hydroxy-dimethylglutaric acid,

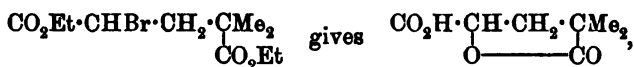


Lastly, the methyl ester of this lactonic acid, when heated with sodium and *iso*amyl alcohol, undergoes molecular change, yielding an *aa*-dimethylglutaconic acid,



which melts at 150°. This acid is unsaturated, since its solution in sodium carbonate readily decolorises permanganate, but it is not known whether dimethylmalonic acid is or is not formed during this oxidation. The author of the present paper is, however, of the opinion that this unsaturated acid obtained by Conrad is not *aa*-dimethylglutaconic acid, because the lactone melting at 153° from which it was obtained does not appear to be the lactone of  $\alpha_1$ -hydroxy-*aa*-dimethylglutaric acid.

It is shown on p. 259 of this paper that the lactone of this constitution is produced in considerable quantities, along with *aa*-dimethylglutaconic acid, by the action of alcoholic potash on ethylic bromodimethylglutarate.



and as thus obtained it is a substance which crystallises well from toluene and melts at 83°, or nearly 70° lower than Conrad's lactone. It must be left to further investigation to determine what the constitution of Conrad's unsaturated acid is.

An acid of the formula of *aa*-dimethylglutaconic acid should, of course, exist in *cis*- and *trans*-modifications corresponding with maleic and fumaric acids, and these may be represented thus :



It is probable that the acid melting at 172°, obtained by the hydrolysis of ethyl bromodimethylglutarate, is the *trans*-modification, because of its high melting point, its sparing solubility in water, and the fact that it is not easily attacked by bromine, and does not yield an anhydride on treatment with acetic anhydride. There can also be little doubt that the acid, of melting point about 133°, obtained by Henrich, is *aa*-dimethylglutaconic acid, not only on account of the way in which it is formed, but also because it yields dimethylmalonic acid on oxidation. Possibly this is a mixture of the *cis*- and *trans*-modifications difficult to separate into its constituents by fractional crystallisation, and experiments are at present being made in order to determine whether this is the case.

Many attempts have been made to convert the acid of melting point 172° into the corresponding *cis*-modification, but these have all failed,

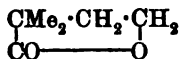
partly on account of the acid not yielding an anhydride, but principally because the acid is so readily decomposed on heating with elimination of carbon dioxide.

This decomposition seemed so interesting that it was carefully investigated, and it is shown on p. 256 that the elimination of carbon dioxide is accompanied by the formation of an oily, unsaturated acid of the formula  $C_8H_{10}O_2$ , which boils at  $207-208^\circ$ .

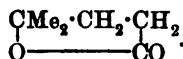
Carbon dioxide may be removed from  $\alpha\alpha$ -dimethylglutaconic acid,  $CO_2H \cdot CMe_2 \cdot CH : CH \cdot CO_2H$ , in two directions, yielding the following unsaturated acids.



Since, however, the acid actually obtained is quantitatively converted into a lactone on treating with 33 per cent. sulphuric acid, it cannot be isopropylacrylic acid, which contains the double linking in the  $\alpha\beta$ -position. It is therefore *vinyldimethylacetic acid*, and the lactone formed by the action of the sulphuric acid is the *lactone* of *hydroxyethyl-dimethylacetic acid*, and is isomeric with the isocapro lactone which has been obtained by the distillation of terebic acid,  $\begin{array}{c} Me_2C - CH \cdot CO_2H \\ | \\ O \cdot CO \cdot CH_2 \end{array}$ , and in other ways.



*Lactone of hydroxyethyl-dimethylacetic acid* (b. p.  $206^\circ$ ).



*isocapro lactone* (b. p.  $207^\circ$ ).

The solution of vinyldimethylacetic acid in chloroform instantly decolorises bromine with formation of *dibromoethyl-dimethylacetic acid*,  $CO_2H \cdot CMe_2 \cdot CHBr \cdot CH_2Br$ , and its unsaturated nature is also shown by the fact that its solution in chloroform instantly reduces permanganate; but, on the other hand, the acid is not acted on by sodium amalgam, a behaviour which has repeatedly been observed in the case of other acids of similar constitution.



The method which was employed in preparing the large quantities of this anhydride which were required for the research was as follows.\* Finely powdered isolaunonic acid (100 grams) is mixed, in a flask of 1500 c.c. capacity, with 500 c.c. of nitric acid (sp. gr. 1.2) and cautiously heated on the water-bath. As soon as the first violent reaction has

\* Compare Blanc (*Bull. Soc. Chim.*, 1898, [iii], 19, 284).

subsided, the heating is continued for about 6 hours, with a further addition of small quantities of nitric acid of the same strength if it is found that the first quantity is not sufficient to dissolve the isolaconic acid completely. The clear solution is evaporated to a small bulk, mixed with water, and the evaporation repeated with the constant addition of small quantities of water, until nearly all the nitric acid has been removed. The residue, after concentrating as far as possible, is allowed to stand, when it gradually becomes converted into a semi-solid mass, owing to the separation of dimethylglutaric acid. After the mother liquor \* has been removed as far as possible on the pump, the residue is left in contact with porous porcelain until quite dry, and then heated to boiling in a reflux apparatus with twice its weight of acetic anhydride for 6 hours. The acetic acid and excess of anhydride are then distilled off and the crude anhydride purified by fractionation under reduced pressure, when, after two distillations, almost the whole quantity distils at 175—180° (60 mm.), and on cooling sets to a mass of crystals. These are transferred to the pump, and the residue left in contact with porous porcelain; the substance then consists of pure *αα*-dimethylglutaric anhydride melting at 38—40°. On analysis:

0.1371 gave 0.2963 CO<sub>2</sub> and 0.0895 H<sub>2</sub>O. C = 59.0; H = 7.3.

C<sub>7</sub>H<sub>10</sub>O<sub>3</sub> requires C = 59.1; H = 7.1 per cent.

*Ethyl Bromodimethylglutarate*, CO<sub>2</sub>Et·CMe<sub>2</sub>·CH<sub>2</sub>·CHBr·CO<sub>2</sub>Et.

In preparing this bromo-ester, dimethylglutaric anhydride (14 grams) is mixed with phosphorus pentachloride (22 grams) in a flask fitted with a ground-in air-tube and the mixture heated to boiling for about 1 hour and until the whole of the pentachloride has dissolved. After cooling, a slight excess of bromine (17 grams) is added and the whole heated on the water-bath for 12 hours. The action of bromine is unusually slow, and it sometimes happens that even after 12 hours the whole of it has not been used up; in such cases, the liquid is sealed up in tubes and heated at 125—130° for 2 hours. The somewhat brownish product is now poured in a thin stream into three times its volume of alcohol, and after the vigorous reaction has subsided, and the whole has become cold, it is poured into a large volume of ice and water. The heavy oil is then extracted twice with ether, the ethereal solution washed with sodium carbonate, dried over calcium chloride, evaporated, and the residual oil rapidly fractionated under reduced pressure, when almost the whole quantity passes over at 165—170°

\* A further quantity of crude dimethylglutaric acid may be obtained from this mother liquor by repeatedly evaporating with water and finally allowing the residue to remain over sulphuric acid until nearly solid.

under 35 mm. pressure and consists of nearly pure *ethyl bromodimethylglutarate*. On analysis :

0.217 gave 0.1325 AgBr. Br = 26.1.

$C_{11}H_{19}BrO_4$  requires Br = 27.1 per cent.

*Action of Alcoholic Potash on Ethyl Bromodimethylglutarate. Formation of aa-Dimethylglutaconic Acid,  $CO_2H \cdot CMe_2 \cdot CH : CH \cdot CO_2H$ .*

When the bromo-ester is digested with a large excess of alcoholic potash, hydrolysis and elimination of hydrogen bromide takes place simultaneously with formation of dimethylglutaconic acid and the lactone of hydroxydimethylglutaric acid (p. 259). The process was usually carried out in the following way.

Caustic potash (35 grams) is dissolved in the least quantity of boiling alcohol in a large flask fitted with a wide condenser, and through the top of this the bromo-ester (50 grams) is run in rapidly from a tap funnel, so that the reaction may be as vigorous as possible and yet sufficiently under control to prevent loss through the liquid being forced out of the condenser. The whole is then boiled on the water-bath for 1 hour, diluted with water, and evaporated with successive additions of water until it is quite free from alcohol ; the strongly alkaline liquid is then mixed with excess of hydrochloric acid and extracted 10 times with ether.

After washing with water, drying over calcium chloride, and distilling off the bulk of the ether, a point is reached in the concentration when crystals begin to separate ; at this stage, the flask is well cooled and shaken, and the crystals collected on the pump and washed with ether.\*

The colourless, crystalline mass consists of almost pure *aa-dimethylglutaconic acid*, and after once crystallising from water, needle-shaped crystals were obtained which melted at 172°. On analysis :

0.1740 gave 0.338  $CO_2$  and 0.1008  $H_2O$ . C = 53.0 ; H = 6.4.

0.1581 „ 0.308  $CO_2$  „ 0.0920  $H_2O$ . C = 53.1 ; H = 6.4.

$C_7H_{10}O_4$  requires C = 53.2 ; H = 6.3.

*aa*-Dimethylglutaconic acid melts at 172°, and is very sparingly soluble in cold water, but dissolves readily on boiling. It is readily soluble in methyl alcohol, acetone, or glacial acetic acid, sparingly in chloroform, ether, or toluene ; even in boiling toluene it is only dissolved to a very slight extent and in this respect it differs from the *aa*-dimethylglutaconic acid prepared by Henrich (p. 249).

The molecular weight of the acid as determined by the boiling point

\* For the description of the treatment of the ethereal mother liquors of these crystals, see p. 259.



method was found to be 146 and 144, whereas the molecular weight of  $C_7H_{10}O_4$  is 158. That the acid is a dibasic acid was shown by titration with decinormal caustic soda when 0.1763 gram neutralised 0.044 gram NaOH, whereas this amount of a dibasic acid,  $C_7H_{10}O_4$ , should neutralise 0.044 gram NaOH.

*$\alpha,\beta$ -Dibromo- $\alpha\alpha$ -dimethylglutaric Acid*,  $CO_2H \cdot CMe_2 \cdot CHBr \cdot CHBr \cdot CO_2H$ ,

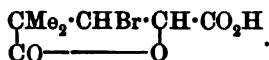
Dimethylglutaconic acid is not readily attacked by bromine, as is shown by the fact that when suspended in chloroform it does not decolorise bromine, but it may be converted into its dibromo-additive product in the following way. The pure acid is ground to a fine powder and mixed with a large excess of bromine, in which it dissolves; the liquid is left overnight in a closed vessel and then poured on to a watch glass and exposed to the air.

After the bromine has evaporated, an almost colourless residue is obtained which crystallises from glacial formic acid in needles and melts at 217—219°. On analysis :

0.1974 gave 0.231 AgBr. Br = 51.7.

$C_7H_{10}O_4Br_2$  requires Br = 50.3 per cent.

*$\alpha,\beta$ -Dibromo  $\alpha\alpha$ -dimethylglutaric acid* is almost insoluble in cold water, benzene, chloroform, and light petroleum, but dissolves readily in methyl alcohol. When the finely powdered substance is boiled with sufficient water, it rapidly dissolves, much hydrogen bromide is eliminated, and the solution, when concentrated to a small bulk, deposits on cooling beautiful, needle-shaped crystals. These, after recrystallising from water, melt at about 168—170°, the fused mass giving off gas rapidly at 180°, and becoming quite black. The crystals are readily soluble in sodium carbonate in the cold, and the solution does not decolorise permanganate in the cold, but on warming reduction sets in at once. The substance contains much bromine and is evidently the lactone of  $\beta$ -bromo- $\alpha_1$ -hydroxy- $\alpha\alpha$ -dimethylglutaric acid,



*Ethyl Dimethylglutaconate*,  $CO_2Et \cdot CMe_2 \cdot CH : CH \cdot CO_2Et$ .

In order to prepare this ester, the pure acid was heated in a reflux apparatus with alcohol and sulphuric acid for 6 hours on the water-bath. The product was mixed with water, extracted three times with ether, the ethereal solution washed well with water and dilute sodium carbonate, and after drying over calcium chloride, the ether evaporated,

when a colourless oil was obtained which distilled constantly at 195—197° (200 mm.).

0.1679 gave 0.3797  $\text{CO}_2$  and 0.1316  $\text{H}_2\text{O}$ .  $\text{C} = 61.7$ ;  $\text{H} = 8.7$ .

$\text{C}_{11}\text{H}_{18}\text{O}_4$  requires  $\text{C} = 61.7$ ;  $\text{H} = 8.4$  per cent.

*Ethyl dimethylglutaconate* is a colourless oil which has a pleasant but pronounced odour closely resembling that of pineapples. It was noticed in its preparation that dimethylglutaconic acid is esterified with great ease, and that only a trace of an acid ester was extracted from the product by means of the sodium carbonate employed.

*Oxidation of aa-Dimethylglutaconic Acid. Formation of Dimethylmalonic Acid and Oxalic Acid.*

In carrying out this oxidation, pure dimethylglutaconic acid (4 grams) was dissolved in a slight excess of sodium carbonate, water (500 c.c.) was added, and after the solution had been mixed with powdered ice, a cold saturated solution of potassium permanganate was run in until the colour, which disappeared instantaneously at first, remained permanent. During the whole operation, a rapid stream of carbon dioxide was passed, and the liquid was also kept well stirred by means of a turbine. The product was decolorised by adding sodium sulphite, heated to boiling, filtered, and the filtrate and the washings of the manganese precipitate were evaporated to a small bulk. The concentrated residue was acidified and extracted ten times with pure ether and the ethereal solution evaporated, when a syrupy acid was obtained which, on examination, was found to contain much oxalic acid, as well as another acid, evidently dimethylmalonic acid, since, on heating, carbon dioxide was evolved and an oily acid smelling of isobutyric acid produced. In order to separate these acids, they were dissolved in water, the solution made strongly alkaline with ammonia, heated to boiling, and then excess of calcium chloride added. After filtering from the calcium oxalate, the filtrate was concentrated and allowed to stand, when a quantity of colourless, star-like crystals separated, which consisted of the calcium salt of dimethylmalonic acid. The crystals were collected, decomposed with hydrochloric acid, and the solution extracted with ether. The ethereal solution was then carefully dried over calcium chloride and evaporated nearly to dryness, when, on standing, glistening, prismatic crystals separated which melted at 190° and consisted of pure *dimethylmalonic acid*:

0.1723 gave 0.2887  $\text{CO}_2$  and 0.0956  $\text{H}_2\text{O}$ .  $\text{C} = 45.7$ ;  $\text{H} = 6.2$ .

0.1206 „ 0.2016  $\text{CO}_2$  „ 0.0669  $\text{H}_2\text{O}$ .  $\text{C} = 45.6$ ;  $\text{H} = 6.1$ .

$\text{C}_8\text{H}_8\text{O}_4$  requires  $\text{C} = 45.5$ ;  $\text{H} = 6.1$  per cent.

As it was most important that there should be no doubt as to the identity of this acid, it was heated in a small retort until the evolution of carbon dioxide had ceased, when an oily acid was produced, which distilled constantly at  $154^{\circ}$  (748 mm.) and consisted of pure *isobutyric acid* :

0.152 gave 0.3022  $\text{CO}_2$  and 0.125  $\text{H}_2\text{O}$ .  $\text{C} = 54.2$  ;  $\text{H} = 9.2$ .

$\text{C}_4\text{H}_8\text{O}_2$  requires  $\text{C} = 54.5$  ;  $\text{H} = 9.1$  per cent.

By weighing the calcium oxalate formed, it was found that the dimethylglutaconic acid had been converted almost quantitatively into oxalic and dimethylmalonic acids by oxidation with permanganate under the conditions given above.

*Distillation of Dimethylglutaconic Acid. Formation of Vinyl dimethylacetic Acid,  $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH} : \text{CH}_2$ .*

Dimethylglutaconic acid (3 grams) was heated in a small retort by means of a metal-bath, when it first melted, and then, at about  $200^{\circ}$ , carbon dioxide commenced to come off in quantity. When the evolution of gas had ceased, the residue, which had a strong odour like that of *isovaleric acid*, was distilled, and nearly the whole quantity passed over at  $195$ — $210^{\circ}$ , only a small quantity of a thick, dark-coloured oil remaining. The distillate, on cooling, deposited a few crystals, consisting probably of a trace of unchanged acid, but after again distilling, a colourless oil passed over almost constantly at  $207$ — $208^{\circ}$  (760 mm.), and this showed no signs of crystallising. On analysis :

0.1186 gave 0.2767  $\text{CO}_2$  and 0.0966  $\text{H}_2\text{O}$ .  $\text{C} = 63.6$  ;  $\text{H} = 9.0$ .

$\text{C}_6\text{H}_{10}\text{O}_2$  requires  $\text{C} = 63.2$  ;  $\text{H} = 8.8$  per cent.

*Vinyl dimethylacetic acid* is a colourless, unpleasant smelling oil, which behaves like an unsaturated acid, since, when dissolved in sodium carbonate, it at once decolorises permanganate at the ordinary temperature ; its solution in chloroform also instantly absorbs bromine.

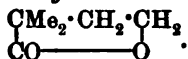
In order to investigate the latter reaction, 1 gram of the acid was dissolved in chloroform, and after cooling in ice water, bromine was added drop by drop until the colour just remained. On exposure to the air in a watch-glass, it was noticed that the liquid gave off a little hydrogen bromide, and after the chloroform had evaporated, a pale yellow oil remained, which when left overnight became semi-solid. In contact with porous porcelain, the dark-coloured mother liquor was rapidly absorbed and a colourless, crystalline mass was left. On analysis :

• 0.0843 gave 0.1141  $\text{AgBr}$ .  $\text{Br} = 60.1$ .

$\text{C}_6\text{H}_{10}\text{O}_2\text{Br}_2$  requires  $\text{Br} = 58.4$  per cent.

This substance is evidently *dibromoethyl dimethylacetic acid*,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , and in its crude state it melted at about  $100^\circ$ . Unfortunately, the quantity was too small to allow of its being recrystallised. Vinyl dimethylacetic acid is apparently not acted on by sodium amalgam, since 1 gram of it, after boiling with excess of sodium amalgam for 1 hour, was recovered unchanged on acidifying and extracting with ether.

*Lactone of Hydroxyethyl dimethylacetic Acid (α-Dimethylbutyrolactone),*

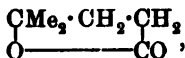


Vinyl dimethylacetic acid dissolves in 33 per cent. sulphuric acid, and if the solution is heated to boiling for a few minutes, an oil separates. The product was cooled well, made alkaline by the careful addition of potassium carbonate, and repeatedly extracted with ether. The ethereal solution was dried over potassium carbonate and evaporated, and the residual oil distilled, when almost the whole quantity passed over constantly at  $205\text{--}206^\circ$ . On analysis :

0.1568 gave 0.3607  $\text{CO}_2$  and 0.1271  $\text{H}_2\text{O}$ .  $\text{C} = 62.7$ ;  $\text{H} = 9.0$ .

$\text{C}_6\text{H}_{10}\text{O}_2$  requires  $\text{C} = 63.2$ ;  $\text{H} = 8.8$  per cent.

The *lactone of hydroxyethyl dimethylacetic acid* has a rather pleasant, fruity odour. It dissolves readily in water, but is reprecipitated on adding potassium carbonate. It is closely related to the lactone of  $\gamma$ -hydroxyisocaproic acid (*isocaprolactone*),



which boils at  $207^\circ$ , and which Fittig and Brecht (*Annalen*, 1880, 200, 58, 259) first obtained by the distillation of terebic acid,  $\text{C}_7\text{H}_{10}\text{O}_4$ .

*Synthesis of isoCamphoronic Acid*,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ .

In carrying out this synthesis, sodium (2 grams) was dissolved in alcohol (30 grams), and the solution of sodium ethoxide thus obtained mixed with ethyl cyanoacetate (13 grams) and allowed to stand for 10 minutes. On adding ethyl dimethylglutaconate (20 grams), it was noticed that there was very little rise of temperature, but the reaction seemed to set in rapidly at  $100^\circ$ , as the sodium compound of ethyl cyanoacetate soon passed into solution and the mass quickly acquired a yellow colour. After heating for 15 hours in a reflux apparatus and allowing to cool, a gelatinous mass was obtained which was mixed with excess of dilute hydrochloric acid and extracted three times with ether. After

washing several times with water and evaporating off the ether, 30 grams of a yellow oil were obtained, which was not fractionated and analysed but at once converted into *isocamphoronic* acid by the following process. The oil is mixed with about twice its volume of 90 per cent. sulphuric acid, in which it dissolves with development of heat but without charring. After standing until cold, the whole is diluted with  $1\frac{1}{2}$  vols. of water and heated to boiling in a reflux apparatus for 6 hours, the hydrolysis being facilitated by removing the condenser from time to time in order to allow the alcohol produced to escape. The brownish liquid on standing overnight becomes filled with a mass of crystals and these, after collecting on the pump and washing with a little water, melt at  $164^{\circ}$  and consist of nearly pure *isocamphoronic* acid. A further considerable quantity in a less pure condition may be obtained from the mother liquors by extraction with ether, evaporating, and leaving the residue, which becomes semi-solid on standing, in contact with porous porcelain.

The crystalline acid obtained in this way was not weighed, but the yield was very considerable, and it is only necessary to recrystallise it once from water in order to obtain it quite pure. On analysis :

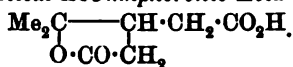
0.1821 gave 0.3341  $\text{CO}_2$  and 0.1064  $\text{H}_2\text{O}$ . C = 50.0 ; H = 6.5.

0.1651 „ 0.3013  $\text{CO}_2$  „ 0.0972  $\text{H}_2\text{O}$ . C = 49.7 ; H = 6.6.

$\text{C}_9\text{H}_{14}\text{O}_6$  requires C = 49.6 ; H = 6.4 per cent.

The synthetical acid, when rapidly heated, softened at  $165^{\circ}$  and melted at  $168^{\circ}$ , whereas the melting point of *isocamphoronic* acid is given as  $166^{\circ}$ . A sample of pure *isocamphoronic* acid from pinene, which Professor A. von Baeyer was good enough to send the author, was mixed with the synthetical acid without any alteration in the melting point being observable. This, and the fact that the synthetical acid on treatment with sulphuric acid yields terpenylic acid, proves that it is identical with the acid obtained from pinene and camphor.

*Conversion of Synthetical isocamphoronic Acid into Terpenylic Acid,*



In carrying out this decomposition, synthetical *isocamphoronic* acid (1 gram) was dissolved in concentrated sulphuric acid (8 grams), and the solution heated at  $100^{\circ}$ , when bubbles of gas were slowly given off. After 6 hours, the liquid, which had scarcely darkened in colour, was diluted with water and repeatedly extracted with ether, the etheral solution was washed until free from sulphuric acid, evaporated, and the oily residue mixed with a very little water and allowed to stand. After about 3 days, the crystals which had separated were left

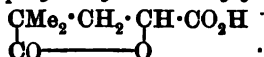
in contact with porous porcelain until dry, and then crystallised from water, when glistening prisms were obtained, which melted at 59—60°, and consisted of hydrated terpenylic acid. On leaving these crystals over sulphuric acid in a vacuum desiccator, they soon became opaque, and after two days the chalky mass melted sharply at 90° and gave the following results on analysis :

0.1634 gave 0.3332 CO<sub>2</sub> and 0.1034 H<sub>2</sub>O. C = 55.6 ; H = 7.0.

C<sub>8</sub>H<sub>12</sub>O<sub>4</sub> requires C = 55.8 ; H = 7.0 per cent.

This acid is therefore terpenylic acid, which, according to Tiemann, crystallises from water in well-defined, hydrated crystals melting at 56° ; these, when placed over sulphuric acid in a vacuum desiccator, lose their water of crystallisation, giving a chalky mass which melts at 90°.

*Lactone of α<sub>1</sub>-Hydroxy-αα-dimethylglutaric Acid,*



The ethereal mother liquors of the crystals of dimethylglutaconic acid (p. 253) yielded on evaporation a thick, brown oil, which, on standing for several days and repeatedly stirring, partially crystallised. The semi-solid mass was spread on porous porcelain and left for some weeks until almost all the thick oil had been absorbed and a yellow, crystalline mass remained. This, after crystallising first from ether and then from water, yielded a considerable quantity of pure dimethylglutaconic acid (m. p. 172°).

The porous plates were crushed and extracted in a Soxhlet apparatus with ether, the ether was then evaporated, and the dark brown oil, from which nothing crystalline could be obtained directly, was esterified by treatment with alcohol and sulphuric acid in the usual way (p. 254). The large amount of ester thus obtained was distilled twice under reduced pressure, and the fraction 215—217° (200 mm.), which was about two-thirds of the whole, collected separately. On boiling this fraction with 10 per cent. hydrochloric acid, it was readily hydrolysed, and on evaporating to dryness a very thick syrup was obtained, which, when placed over sulphuric acid in a vacuum desiccator, soon began to crystallise, and ultimately became almost solid. In contact with porous porcelain, the mother liquor was slowly absorbed, and a colourless, crystalline residue was obtained, which consisted of the *lactone* of *hydroxy-dimethylglutaric acid* mixed with small quantities of dimethylglutaconic acid.

The separation of these two substances is very tedious, and was carried out by rubbing the crystalline mass with 50 per cent. hydrochloric acid, which dissolves the lactone, but in which the dimethyl

glutaconic acid is practically insoluble. After filtering, the filtrate was extracted with ether, the oil obtained after distilling off the ether allowed to solidify, and again treated with hydrochloric acid. Ultimately, the lactone was further purified by recrystallisation from toluene. On analysis:

0.1631 gave 0.3177  $\text{CO}_2$  and 0.0950  $\text{H}_2\text{O}$ .  $\text{C} = 53.1$ ;  $\text{H} = 6.4$ .

0.1304 „ 0.2544  $\text{CO}_2$  „ 0.0760  $\text{H}_2\text{O}$ .  $\text{C} = 53.2$ ;  $\text{H} = 6.5$ .

$\text{C}_7\text{H}_{10}\text{O}_4$  requires  $\text{C} = 53.1$ ;  $\text{H} = 6.3$  per cent.

The lactone of  $\alpha_1$ -hydroxy- $\alpha\alpha$ -dimethylglutaric acid melts at about  $85^\circ$  but not quite sharply. It is readily soluble in water, and when the crystals are placed on water they rotate rapidly, like camphor crystals, and slowly dissolve. The lactone dissolves readily in hot toluene, but is sparingly soluble in the cold.

That it is a monobasic lactonic acid is shown by its behaviour on titration with decinormal caustic soda solution, when 0.1849 gram, dissolved in cold water, neutralised 0.049 gram  $\text{NaOH}$ , whereas this amount of a monobasic acid,  $\text{C}_7\text{H}_{10}\text{O}_4$ , should neutralise 0.047 gram  $\text{NaOH}$ . A considerable excess of decinormal caustic soda was then added, and the solution heated to boiling for 10 minutes, and the excess of soda estimated by titration with decinormal sulphuric acid. It was then found that the total amount of  $\text{NaOH}$  taken up was 0.0944 gram, whereas 0.1849 gram of a monobasic lactone acid,  $\text{C}_7\text{H}_{10}\text{O}_4$ , on dissolving to form the salt of the hydroxy-dibasic acid, should neutralise 0.094 gram  $\text{NaOH}$ . The first results of titration in the cold show that the lactone ring is hydrolysed only to a very slight extent when the lactonic acid is dissolved in cold water.

The hydroxy-dibasic acid, when set free from its solution in caustic alkali, is obtained on extraction with ether as a colourless syrup, which does not rapidly pass into the lactone, since titration showed that even after standing for a quarter of an hour it consisted principally of the hydroxy-dibasic acid. When, however, the syrup is placed over sulphuric acid in a vacuum desiccator, it is rapidly converted into the lactone and solidifies completely.

*Silver Salt of the Lactone of Hydroxydimethylglutaric Acid,  $\text{C}_7\text{H}_9\text{O}_4\text{Ag}$ .*—When silver nitrate is added to a neutral solution of the ammonium salt, there is at first no precipitate, but soon the silver salt begins to separate in microscopic needles, and when dried it has the appearance of a silky mass of needles, which are readily soluble in hot, but sparingly in cold, water. On analysis:

0.2310 gave 0.2691  $\text{CO}_2$ , 0.0714  $\text{H}_2\text{O}$  and 0.0941  $\text{Ag}$ .  $\text{C} = 31.8$ ;

$\text{H} = 3.4$ ;  $\text{Ag} = 40.7$ .

$\text{C}_7\text{H}_9\text{O}_4\text{Ag}$  requires  $\text{C} = 31.7$ ;  $\text{H} = 3.4$ ;  $\text{Ag} = 40.7$  per cent.

The neutral solution of the ammonium salt gives no precipitate with calcium or barium chlorides, or with copper sulphate or lead acetate.

The author wishes to express his thanks to Mr. J. Yates for his valuable assistance in carrying out this investigation, and also to state that some of the expense of the research was met by repeated grants from the Research Fund of the Royal Society.

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## XXVI.—*Tetrazoline. Part II.*

By SIEGFRIED RUHEMANN and H. E. STAPLETON.

HANTZSCH and SILBERRAD, in their interesting research on diazoacetic ester (*Ber.*, 1900, 33, 58), showed that one of the polymerides of diazomethanes, described by Curtius and Lang (*J. pr. Chem.*, 1888, [ii], 38, 534) as trimethintriazimide, was hydrotetrazine (tetrazoline), and they used for its synthesis the same method, namely, the action of heat on monoformylhydrazine, which we had published previously (*Trans.*, 1899, 75, 1131). The remarkable properties of tetrazoline induced us to subject it to a closer study. Although this is not yet completed, we thought it advisable to give a record of the results already arrived at in order to be able to continue the work undisturbed.

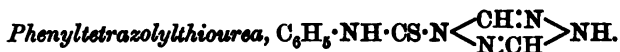
Our attention was mainly directed to the investigation of the action of methyl iodide on tetrazoline. We expected that the basic character of this substance, as indicated by the fact that it forms salts with strong acids and, as stated in this paper, yields a thiourea with phenylhydrazine, would also appear in its behaviour towards alkyl iodides. We were, however, surprised to find that the action of methyl iodide on tetrazoline was complicated and yielded several products, two of which we were able to isolate. One of these is rather unstable, crystallises in dark blue needles, and has the formula  $C_3H_7N_4I_3$ , whilst the other forms colourless crystals, and has the composition  $C_3H_7N_4I$ . The formula of the latter compound would correspond with the iodide of methyltetrazoline; its behaviour, however, proves it to have another constitution, for, on attempting to isolate the base from the iodide or the chloride by means of an alkali or silver oxide, oxidation takes place, and a deep blue solution is produced, whereas tetrazoline does not give a similar reaction. More remarkable still is the nature of the other compound which is formed from tetrazoline and methyl iodide. It is decomposed with separation



of iodine even by cold water, more readily, however, on boiling; this property characterises it as a nitrogen iodide.

The continuation of this research, which one of us has undertaken, will most probably lead to the knowledge of the reaction between methyl iodide and tetrazoline, and to the establishment of the constitutional formulæ of the two compounds which are described in this paper.

#### EXPERIMENTAL.



A mixture of tetrazoline and phenyl mustard oil, when cautiously heated, yields an oil which, on adding a little dilute alcohol, sets to a white solid. In order to remove the adhering mustard oil, it is washed with ether and then dissolved in boiling alcohol, from which, on cooling, it separates in colourless needles melting at 153–154°. On analysis:

0.1457 gave 39.4 c.c. moist nitrogen at 16° and 774 mm.  $N = 32.15$ .

0.2040 „ 0.2219  $BaSO_4$ .  $S = 14.93$ .

$C_9H_9N_4S$  requires  $N = 31.96$ ;  $S = 14.61$  per cent.

#### *Action of Methyl Iodide on Tetrazoline.*

On heating tetrazoline with an excess of methyl iodide at 100° in a closed tube for 3 hours, a dark red, viscous product is formed which is freed from the unaltered alkyl iodide by evaporation on the water-bath. After adding a few drops of methyl alcohol, the oil is allowed to remain in a desiccator over sulphuric acid, when, in the course of a day, a solid separates. This is filtered and dissolved in a warm mixture of chloroform and alcohol, from which, on cooling, bluish-black needles crystallise melting at 102–103°. The following analytical data of the substances, dried in vacuo, correspond with the formula  $C_8H_9N_4I_3$ :

0.2258 gave 0.0655  $CO_2$  and 0.0382  $H_2O$ .  $C = 7.91$ ;  $H = 1.87$ .

0.2395 „ 0.0660  $CO_2$  „ 0.0380  $H_2O$ .  $C = 7.51$ ;  $H = 1.76$ .

0.2534 „ 24.5 c.c. moist nitrogen at 10° and 767 mm.  $N = 11.68$ .

0.2243 „ 0.3242  $AgI$ .  $I = 78.11$ .

0.2453 „ 0.3578  $AgI$ .  $I = 78.81$ .

$C_8H_9N_4I_3$  requires  $C = 7.47$ ;  $H = 1.87$ ;  $N = 11.62$ ;  $I = 79.04$  per cent.

The substance is soluble in cold alcohol, and the solution gives with silver nitrate a precipitate of silver iodide, which proves it to be an iodide. Carbon disulphide neither dissolves it nor is it coloured by it; the characteristic violet coloration, due to iodine, appears, however,

on adding a trace of water. This fact indicates that the compound is a nitrogen iodide, and that water has to be excluded in its preparation. More readily than with cold water does the decomposition take place on boiling. The substance melts, and iodine is separated which distils with the steam. The dark solution which remains, and which is almost neutral to litmus paper, is freed from iodine by extraction with carbon disulphide, and, on concentration, yields a dark oil which does not deposit crystals, even on standing for several days. The viscous residue, when heated with potash, decomposes and evolves ammonia; we have not been able to isolate any other substance.

The yellowish mother liquor from the bluish-black needles contains the second compound which is formed by the action of methyl iodide on tetrazoline. It is evaporated on the water-bath, and the dark oil which remains, on standing in vacuo over sulphuric acid, yields slightly coloured crystals. A further crop can be obtained from the syrupy filtrate; finally, a viscous product is left behind from which nothing crystalline separates. The compound, after recrystallisation from water or methyl alcohol, appears in well developed, colourless crystals which melt at 98–99°, and on analysis yield data which agree with the formula  $C_3H_7N_4I$ .

0.2166 gave 0.1268  $CO_2$  and 0.0605  $H_2O$ .  $C = 15.96$ ;  $H = 3.10$ .

0.2405 „ 51 c.c. moist nitrogen at 13° and 750 mm.  $N = 24.71$ .

0.1597 „ 0.1634 AgI.  $I = 55.38$ .

0.2063 „ 0.2135 AgI.  $I = 55.93$ .

$C_3H_7N_4I$  requires  $C = 15.92$ ;  $H = 3.09$ ;  $N = 24.77$ ;  $I = 56.19$  per cent.

This compound is almost insoluble in chloroform, but dissolves with the greatest ease in alcohol or water. It can be transformed into the corresponding chloride by boiling its aqueous solution with an excess of freshly prepared silver chloride. The filtrate is evaporated on the water-bath, when an oil is left behind which solidifies on standing in vacuo over sulphuric acid for a day. The chloride is extremely soluble in water, less so in absolute alcohol, and crystallises from it in deliquescent, colourless needles which melt at 130°. On analysis:

0.3153 gave 0.3305 AgCl.  $Cl = 25.93$ .

$C_3H_7N_4Cl$  requires  $Cl = 26.39$  per cent.

The concentrated aqueous solution of the chloride gives with platinic chloride beautiful, red plates of the platinichloride which is rather soluble in cold, readily in boiling, water, but is almost insoluble in cold absolute alcohol, and melts at 175°. On analysis:

0.2415 left, on ignition, 0.0775 Pt.  $Pt = 32.09$ .

$(C_3H_7N_4)_2H_2PtCl_6$  requires  $Pt = 32.11$  per cent.

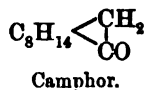
The formation of a platinichloride leads to the view that the substance  $C_8H_7N_4Cl$  is not the hydrochloride of methyltetrazoline, since tetrazoline itself yields a compound of the formula  $(C_2H_4N_4)_2PtCl_4$ . This conclusion is supported by the fact that solutions of the chloride or the iodide in the presence of an alkali turn violet on exposure to the atmosphere, but that such a reaction does not take place with tetrazoline. On account of the solubility of the base in water, and the ease with which it is oxidised, we have not succeeded in isolating it, since silver oxide has not the desired effect; neither have we been able, as yet, to obtain the blue oxidation product in a pure state.

GONVILLE AND CAIUS COLLEGE,  
CAMBRIDGE.

XXVII.—*Studies in the Camphane Series. Part VII.*  
*Conversion of Hydroxycamphene into  $\beta$ -Halogen Derivatives of Camphor.*

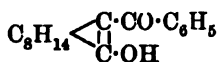
By MARTIN ONSLOW FORSTER.

IN a recent communication (Trans., 1901, 79, 644) I described, under the name hydroxycamphene, an isomeride of camphor which exhibited some remarkable properties. The method by which it was obtained from camphor, although circuitous, leads by steps, apparently straightforward, through camphoroxime, bromonitrocaphane, nitrocaphane, and aminocaphane. The substance itself behaves like an unsaturated compound towards bromine and potassium permanganate, and is readily converted into camphor by the agency of dilute mineral acids; it also contains the hydroxyl group. On the strength of these facts, it was regarded as the tautomeric modification of camphor:

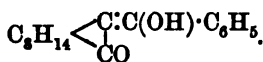


It was necessary to admit, however, that in some respects the behaviour of hydroxycamphene was dissimilar from that which is usually associated with compounds of this type. Its unsaturated character, and its ready conversion into the ketonic isomeride were certainly in accordance with this view of its constitution, but its insolubility in alkalis, the indifference of an alcoholic solution towards ferric chloride, and the extraordinary stability of the substance on distillation, were

points which demanded an explanation more complete than that which was put forward at the time. It was suggested, namely, that the abnormal behaviour of hydroxycamphene might be due to the fact that, unlike the enolic modifications of the ketonic esters which have received so much attention during recent years, it contains no acyl substituent attached to the  $\beta$ -carbon atom. This view received some support from the observation (Trans., 1901, 79, 987) that  $\alpha$ -benzoylcamphor, in which the acyl radicle occupies a  $\beta$ -position relative to the ketonic oxygen, is readily converted into an enolic modification which has all the general properties of compounds belonging to this class. On the other hand, it must be borne in mind that the constitution of enolic  $\alpha$ -benzoylcamphor is by no means assured, because although, at present, the evidence is in favour of representing it as 1-hydroxy-2-benzoylcamphene, the matter is still under investigation, which may produce facts in support of the alternative structure, namely, that of phenylhydroxymethylenecamphor:

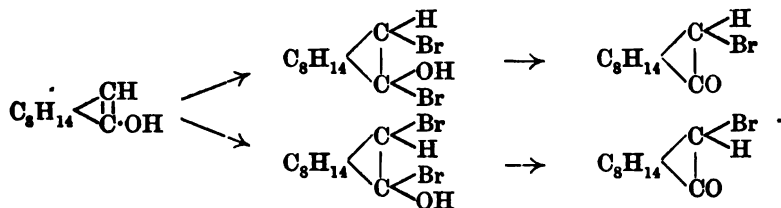


1-Hydroxy-2-benzoylcamphene.



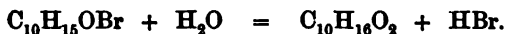
Phenylhydroxymethylenecamphor.

With the object of gaining further evidence relating to the constitution of hydroxycamphene, the action of bromine on this compound has been studied. It was anticipated that if the structure of hydroxycamphene is that which has been assigned to it, addition of bromine, followed by elimination of hydrogen bromide, would yield  $\alpha$ -bromocamphor, either alone, or mixed with the unknown  $\alpha'$ -bromocamphor:



The product actually obtained by the action of bromine on hydroxycamphene {dissolved in glacial acetic acid containing sodium acetate} is a new bromocamphor, which melts at  $78^\circ$ , and when dissolved in alcohol has  $[\alpha]_D +19^\circ$ ;  $\alpha$ -bromocamphor melts at  $76^\circ$  and has  $[\alpha]_D +135^\circ$ . No addition to the list of mono-halogen derivatives of camphor has been made since Kipping and Pope described  $\pi$ -chlorocamphor and  $\pi$ -bromocamphor (Trans., 1895, 67, 371), prepared by eliminating sulphur dioxide from camphorsulphonic chloride and bromide respectively. Since the new bromocamphor does not agree in properties with those attributed to any of the isomerides previously

described, it seemed probable at first that it was  $\alpha'$ -bromocamphor, the unknown stereoisomeride of ordinary  $\alpha$ -bromocamphor. Such a substance, however, would be expected to yield  $\alpha$ -bromocamphor on treatment with the usual transforming agents, but the new derivative resists the action of fuming hydrogen bromide and concentrated sulphuric acid. Moreover, alcoholic potash should convert it into camphor, and although zinc and acetic acid reduce it to that substance, showing it to be a true camphor derivative, alcoholic potash acts as a hydrolytic agent, giving rise to  $\alpha$ -campholenic acid:



Finally, bromine, which would yield  $\alpha$ -dibromocamphor in the case of  $\alpha'$ -bromocamphor, converts the new substance into  $\beta$ -dibromocamphor.

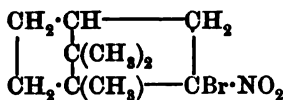
These facts have only one explanation. The substance obtained by the action of bromine on hydroxycamphene must be the unknown  $\beta$ -bromocamphor, bearing the relation to  $\beta$ -dibromocamphor that  $\alpha$ -bromocamphor has to  $\alpha$ -dibromocamphor. In the last-named substance both bromine atoms occupy the  $\alpha$ -position, whilst in  $\beta$ -dibromocamphor, which is more suitably named  $\alpha\beta$ -dibromocamphor, one bromine atom is attached to the  $\alpha$ -carbon atom, the other occupying the  $\beta$ -position, of which the exact situation is unknown.

A bromo-derivative of camphor has been described by Marsh, who refers to the substance as " $\beta$ -bromocamphor." Without disparaging the claims of this compound to be regarded as an individual substance, it may be questioned whether the bromine atom occupies the  $\beta$ -position in the sense just indicated, it being nowhere stated that bromine converts it into  $\alpha\beta$ -dibromocamphor, or that alcoholic potash resolves it into  $\alpha$ -campholenic acid.

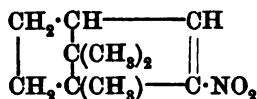
It will be recognised that the production of  $\beta$ -bromocamphor from hydroxycamphene by a process so simple as addition of bromine followed by elimination of hydrogen bromide, necessitates a reconsideration of the relationship between camphor and hydroxycamphene. The last-named substance is indifferent towards hydroxylamine and phenylhydrazine, but readily forms alkyl ethers; its hydroxylic character seems therefore assured, apart from the fact that it is produced by the action of nitrous acid on a primary amine. There is no reason to doubt that the nitro-group in 1:1-bromonitrocamphane, and consequently the nitro-group in nitrocamphene, and the amino-group in aminocamphene, are attached to the carbon atom which, in camphor, is ketonic, because bromonitrocamphane yields camphoroxime on reduction, and aminocamphene gives rise to camphor when heated with acetic anhydride; moreover, hydroxycamphene is converted so readily into camphor that the action of nitrous acid on aminocamphene can scarcely have been abnormal. The only uncertain step, therefore,

in the series connecting camphoroxime with hydroxycamphene, is the removal of hydrogen bromide from 1:1-bromonitrocamphane. The question arises, How does this change take place?

Adopting Breddt's formula for camphor as the basis of representation, the constitution of 1:1-bromonitrocamphane is expressed as follows :

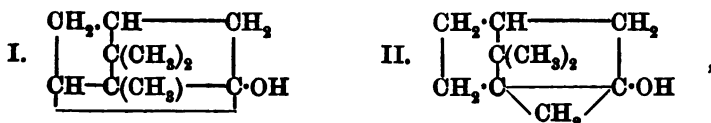


The point to be decided, therefore, is the source of the hydrogen atom which is eliminated in association with bromine when bromonitrocamphane is converted into nitrocamphene. In view of the unsaturated character of the latter, and the fact that, of the two carbon atoms united with that to which the bromine is attached, only one is combined with hydrogen, it was natural to conclude that nitrocamphene is represented by the formula :

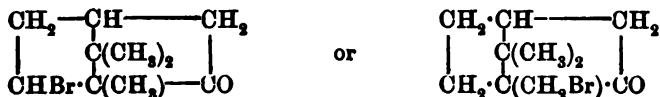


It is this expression which is now shown to be incorrect. It is, however, the sole possible formula for a compound which is not only produced by the removal of hydrogen bromide from 1:1-bromonitrocamphane, but also contains an ethylenic link. The obvious conclusion is that nitrocamphene, and consequently hydroxycamphene, are compounds which owe their unsaturated nature to a trimethylene or tetramethylene ring, which is resolved so easily into the original form as to simulate an ethylenic structure.

Although, theoretically, this change might occur in each of six ways, the production of  $\alpha$ -campholenic acid by the action of alcoholic potash on  $\beta$ -bromocamphor renders all improbable excepting two; these would involve the representation of hydroxycamphene by one of the formulæ :

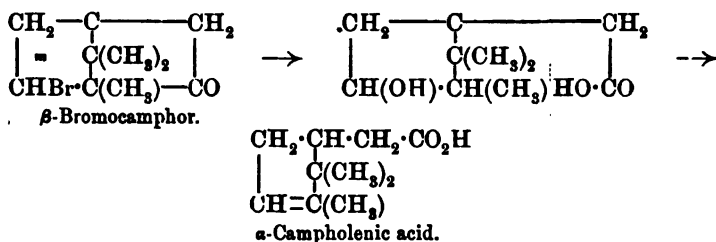


the structure of  $\beta$ -bromocamphor being then indicated by one of the expressions :

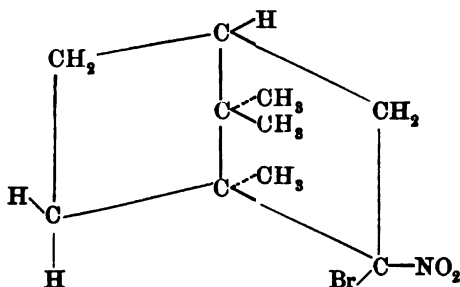


respectively.

So far as the evidence in this paper is concerned, it is scarcely possible to come to a definite conclusion, although the transformation of  $\beta$ -bromocamphor into  $\alpha$ -campholenic acid is distinctly in favour of the former representation, according to which the change in question, although fundamental, would appear quite simple, as follows:



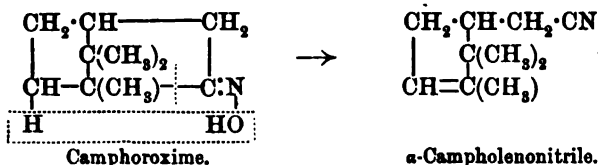
Moreover, although the plane formula I represents union to have occurred between two carbon atoms which appear to be at some distance from one another, it is possible that they are in reality comparatively close, in accordance with the tetrahedral conception of the combining power of carbon. This is illustrated by the following representation of bromonitrocamphane:



Simultaneously with the publication of a preliminary notice of  $\beta$ -bromocamphor (Proc., 1901, 243, 245), Armstrong and Lowry recorded the properties of the same substance obtained by the action of heat on the camphorsulphonic bromide belonging to the Reychler series. These authors have converted  $\beta$ -bromocamphor by direct oxidation into  $\beta$ -bromocamphoric acid, and the investigation of the latter should make it possible to determine which, if either, of the two formulæ suggested in this paper correctly represents the constitution of  $\beta$ -bromocamphor.

An examination of  $\beta$ -bromocamphoroxime has already produced two observations of some interest. In the first place, the oxime does not yield the nitrile of an unsaturated acid when treated with hot dilute sulphuric acid, thereby differing completely from camphoroxime, which is converted into  $\alpha$ -campholenonitrile. This again may be construed in

favour of the expression for  $\beta$ -bromocamphor corresponding with formula I for hydroxycamphene, as it accords with the simplest possible explanation of the last-named reaction:



In the second place, although  $\beta$ -bromocamphor is hydrolysed to  $\alpha$ -campholenic acid by alcoholic potash, this agent is without action on  $\beta$ -bromocamphoroxime, a result which seems to suggest that, in the change undergone so readily by  $\beta$ -bromocamphor, disruption of the ring precedes replacement of bromine by hydroxyl, and the subsequent elimination of water. Indirectly, this also favours the formula for  $\beta$ -bromocamphor in which the bromine is represented as replacing hydrogen in the ring, because if substitution had occurred in a methyl group, it would be reasonable to expect the halogen to be more easily removed.

#### EXPERIMENTAL.



Twenty-five grams of 1-hydroxycamphene were dissolved in 400 c.c. of glacial acetic acid containing 25 grams of anhydrous sodium acetate. To the well cooled liquid were added in small quantities 26.5 grams of bromine dissolved in 100 c.c. of glacial acetic acid; the colour of the halogen was immediately destroyed, and heat being developed, the temperature of the liquid was allowed to return to about 20° before each addition of bromine. When the stated quantity had been added, the pale yellow liquid was poured into a large volume of cold water, which precipitated a colourless, crystalline substance. This was filtered, washed with water, and dried in the desiccator, when it weighed 38 grams.

$\beta$ -Bromocamphor dissolves very readily in warm petroleum, and after being recrystallised twice from this solvent, melts at 78°, the second crystallisation producing no change in the specific rotatory power, and a very slight increase only in the fusion temperature. If the substance, purified in this way, is then recrystallised from absolute alcohol, the melting point is lowered about 1°.

0.2053 gave 0.1656 AgBr. Br = 34.32.

$\text{C}_{10}\text{H}_{15}\text{OBr}$  requires Br = 34.63 per cent.



The substance dissolves very readily in chloroform, benzene, or glacial acetic acid, also in warm petroleum or hot alcohol, crystallising from the last solvent named in long, striated prisms; when deposited slowly by petroleum, it crystallises in large, well formed, transparent prisms. It is readily volatile in steam, the vapour having a faint odour of camphor.

A solution containing 0.5014 gram in 25 c.c. of chloroform at 20°, gave  $\alpha_D$  39' in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D + 16.2^\circ$ ; 0.5012 gram dissolved in 25 c.c. of absolute alcohol at 20°, gave  $\alpha_D$  46' in the same tube, corresponding with  $[\alpha]_D + 19.1^\circ$ .

$\beta$ -Bromocamphor may be dissolved in fuming hydrobromic acid (sp. gr. 1.83) or in concentrated sulphuric acid without undergoing any chemical change or alteration of rotatory power.

*Conversion into Camphor.*—Two grams of  $\beta$ -bromocamphor were dissolved in glacial acetic acid and treated with 5 grams of zinc dust. After remaining on the water-bath during 2 hours, the liquid was diluted with water, neutralised with sodium carbonate, and distilled in a current of steam. Camphor was deposited in the condenser, and was converted into the oxime by the usual process; the product was crystallised from petroleum, which deposited the characteristic crystals melting at 118°.

*Conversion into  $\alpha\beta$ -Dibromocamphor.*—Five grams of the new bromocamphor were covered with one molecular proportion of bromine and heated on the water-bath, when evolution of hydrogen bromide soon occurred. When this gas was no longer liberated, the pale yellow liquid solidified almost immediately on being withdrawn from the water-bath. The product was washed with water, and recrystallised several times from alcohol, until the melting point was constant at 114°, when a mixture of the substance with  $\alpha\beta$ -dibromocamphor melted at the same temperature; 1.0005 gram dissolved in 25 c.c. of chloroform at 21° gave  $\alpha_D$  8°4' in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D + 100.8^\circ$ .

#### *Action of Alcoholic Potash on $\beta$ -Bromocamphor.*

Twenty grams of recrystallised  $\beta$ -bromocamphor were dissolved in 100 c.c. of alcohol which had been distilled from caustic soda; 15 grams of caustic potash, dissolved in the minimum quantity of water, were then added to the liquid, which was heated in a reflux apparatus during 8 hours. Alcohol was then removed by distillation, and a current of steam passed through the residual liquid, a preliminary experiment having shown that if an insufficient quantity of alkali has been employed any bromocamphor remaining unchanged can be removed conveniently at this stage. The contents of the distilling flask were

then cooled, just acidified with dilute sulphuric acid, and extracted with ether, the extract being washed several times with water, dried with calcium chloride, and evaporated on the water-bath. The residue was then distilled, passing over completely at 256—257° under 767 mm. pressure:

0.1570 gave 0.4087 CO<sub>2</sub> and 0.1330 H<sub>2</sub>O. C = 71.00; H = 9.41.

C<sub>10</sub>H<sub>16</sub>O<sub>2</sub> requires C = 71.43; H = 9.52 per cent.

The substance is slowly volatile in steam, and has a very faint odour; it dissolves in sodium carbonate, forming a solution which immediately decolourises potassium permanganate. It has a sp. gr. 0.9974 at 20°/20°, and gives α<sub>D</sub> 16°40' in a 2-dcm. tube at 20°, whence the specific rotatory power [α]<sub>D</sub> + 8.34°. The product was thus identified with α-campholenic acid.



Ten grams of β-bromocamphor were dissolved in 50 c.c. of alcohol and heated with 5 grams of hydroxylamine hydrochloride and 5 grams of dry sodium acetate in a reflux apparatus during 2 hours; 3 grams of the hydrochloride and the same quantity of sodium acetate were then added, and the heating continued during 3 hours, a preliminary experiment having shown that conversion into the oxime is incomplete unless a considerable excess of the hydrochloride is employed. On pouring the liquid into twice its own volume of cold water, a crystalline precipitate was obtained; this was filtered, washed, and recrystallised twice from hot alcohol, which deposited lustrous, rhomboidal plates melting at 156°:

0.2566 gave 0.1944 AgBr. Br = 32.23:

C<sub>10</sub>H<sub>16</sub>ONBr requires Br = 32.52 per cent.

The oxime is readily soluble in chloroform, benzene, or ethyl acetate, but dissolves very sparingly in hot petroleum, which deposits it in aggregates of rhomboidal plates.

A solution containing 0.5017 gram in 25 c.c. of chloroform at 21° gave α<sub>D</sub> - 2°57' in a 2-dcm. tube, whence the specific rotatory power [α]<sub>D</sub> - 73.5°.

β-Bromocamphoroxime dissolves in caustic alkalis and in 50 per cent. sulphuric acid; it may be warmed with concentrated sulphuric acid without undergoing conversion into a nitrile. It is also indifferent to alcoholic potash, with which a specimen has been heated in a reflux apparatus during 4 hours without becoming hydrolysed.

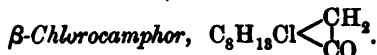
The benzoyl derivative is readily obtained by the Schotten-Baumann method. It is very readily soluble in hot alcohol, from which it

separates in tufts of white needles. Warm petroleum dissolves it less readily, and it is scarcely soluble in the cold solvent, which deposits it in long, snow-white, silky needles melting at 71—73°.

0.2695 gave 0.1437 AgBr. Br = 22.69.

$C_{17}H_{20}O_2NBr$  requires Br = 22.86 per cent.

The substance dissolves very readily in chloroform, ethyl acetate, or benzene. A solution containing 0.5040 gram in 25 c.c. of chloroform at 21° gave  $\alpha_D - 1^\circ 35'$ , whence the specific rotatory power  $[\alpha]_D - 39.2^\circ$ .



Twenty grams of hydroxycamphene were dissolved in 400 c.c. of glacial acetic acid containing 20 grams of anhydrous sodium acetate. The liquid was immersed in cold water and treated with a solution of chlorine in glacial acetic acid, which was added in small quantities at a time until, after an interval, the halogen was found to be in slight excess. As the precipitate obtained on pouring the liquid into a large volume of water weighed only 16 grams, the filtrate was neutralised with solid sodium carbonate, 6 grams more being obtained in this way; the product was then recrystallised three times from alcohol.

0.2064 gave 0.1565 AgCl. Cl = 18.76.

$C_{10}H_{15}OCl$  requires Cl = 19.03 per cent.

The new chlorocamphor is very similar to the bromo-derivative in appearance and properties; it melts, however, at 132.5°. It is readily soluble in chloroform, acetic acid, petroleum, benzene, or ethyl acetate, but dissolves less freely in alcohol, from which it crystallises in slender, striated prisms, sometimes exceeding an inch in length; it is readily volatile in steam, and the vapour has a faint odour of camphor.

A solution containing 0.5012 gram in 25 c.c. of chloroform at 21° gave  $\alpha_D 1^\circ 35'$  in a 2-dm. tube, whence the specific rotatory power  $[\alpha]_D + 39.5^\circ$ ; 0.5019 gram dissolved in 25 c.c. of absolute alcohol at 19° gave  $\alpha_D 1^\circ 38'$ , corresponding to  $[\alpha]_D + 40.7^\circ$ .



The oxime of  $\beta$ -chlorocamphor was obtained by the same process as the bromo-derivative, which it closely resembles in appearance and properties. It separates from alcohol in colourless crystals isomorphous with those of  $\beta$ -bromocamphoroxime, and melts at 134°.

0.2412 gave 0.1662 AgCl. Cl = 17.05.

$C_{10}H_{15}ONCl$  requires Cl = 17.62 per cent.

It dissolves very readily in chloroform, ethyl acetate, or benzene, but is sparingly soluble in boiling light petroleum, from which it crystallises on cooling. A solution containing 0.5015 gram dissolved in 25 c.c. chloroform at 21° gave  $\alpha_D - 2^\circ 20'$  in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D - 58.1^\circ$ . The *benzoyl* derivative was prepared by the Schotten-Baumann method; it dissolves very readily in alcohol and in warm petroleum, crystallising from the latter in lustrous, silky needles, which begin to shrink about 70°, and melt at 86°.

A solution containing 0.5012 gram dissolved in 25 c.c. of chloroform at 21° gave  $\alpha_D - 1^\circ 9'$  in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D 28.7^\circ$ .



Five grams of  $\beta$ -chlorocamphor were heated with 5 grams of bromine in an open flask on the water-bath, when, after a short interval, hydrogen bromide was evolved. Heating was continued until the gas was no longer liberated, the pale yellow liquid solidifying to a camphor-like mass on cooling; this was washed with water until free from acid, dried in the desiccator, and crystallised from a small quantity of boiling petroleum, in which it dissolves readily. After being recrystallised several times from this solvent, it was obtained in tabular aggregates of white prisms, melting at 101°.

0.1445 gave 0.1790 AgCl + AgBr.  $Cl + Br = 43.15$ .

$C_{10}H_{14}OClBr$  requires  $Cl + Br = 43.50$  per cent.

The substance dissolves very readily in cold ethyl acetate, benzene, or chloroform; also in hot alcohol, from which it crystallises in well-formed, oblong prisms. A solution containing 0.5021 gram in 25 c.c. of chloroform at 20° gave  $\alpha_D 5^\circ 5'$  in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D + 126.5^\circ$ .

#### *Ethers of 1-Hydroxycamphene.*

Further evidence of the hydroxylic character of hydroxycamphene was obtained by converting it into ethers, the method which has been studied by Lander (Trans., 1900, 77, 729) having been found very suitable for this purpose.

The *methyl ether*,  $C_{10}H_{15} \cdot OCH_3$ , was prepared by treating 15 grams of hydroxycamphene, dissolved in 45 grams of methyl iodide, with 35 grams of dried silver oxide; no apparent action took place in the cold, and the mixture was therefore heated in a reflux apparatus on the

water-bath during 8 hours. The product was then filtered, and the residue washed several times with dry ether, which was afterwards removed by evaporation. The residual oil was heated with a further quantity of methyl iodide (30 grams) and silver oxide (24 grams) during a period of 8 hours, and subsequently, after removing excess of methyl iodide and the ether employed in washing the silver residue, distilled under the ordinary pressure.

The substance obtained in this manner is a colourless, limpid oil, readily volatile in steam, and having a pleasant odour. It boils at  $193\text{--}194^\circ$  under 766 mm. pressure, has the sp. gr. 0.9314 at  $20^\circ/20^\circ$ , and gives  $\alpha_D - 50^\circ 53'$  in a 2-dm. tube at  $20^\circ$ , whence the specific rotatory power  $[\alpha]_D - 27.31^\circ$ ; a solution containing 0.5012 in 25 c.c. of benzene at  $20^\circ$  gave  $\alpha_D - 58'$  in the same tube, corresponding with  $[\alpha]_D - 24.5^\circ$ .

0.1621 gave 0.4743  $\text{CO}_2$  and 0.1531  $\text{H}_2\text{O}$ . C = 79.80; H = 10.50.

$\text{C}_{11}\text{H}_{18}\text{O}$  requires C = 79.52; H = 10.84 per cent.

A solution of methoxycamphene in chloroform decolorises bromine immediately in the cold.

The *ethyl ether*,  $\text{C}_{10}\text{H}_{15}\cdot\text{OC}_2\text{H}_5$ , was obtained by the same process from hydroxycamphene and ethyl iodide; it boils at  $203\text{--}204^\circ$  under a pressure of 760 mm.

An attempt to hydrolyse the substance with alcoholic potash was unsuccessful, a specimen which was heated with that agent during several hours in a reflux apparatus remaining unchanged.

Bromine converts ethoxycamphene into  $\beta$ -bromocamphor. Five grams were dissolved in glacial acetic acid containing sodium acetate and treated with bromine in the same solvent; on pouring the liquid into water, a crystalline precipitate was obtained, and this, when recrystallised from petroleum, melted at  $78^\circ$ .

An attempt to prepare the benzoyl derivative of hydroxycamphene by the action of benzoyl chloride (2 mols.) on the hydroxy-compound dissolved in pyridine (3 mols.) gave rise to a pale yellow, viscous oil, which did not crystallise.

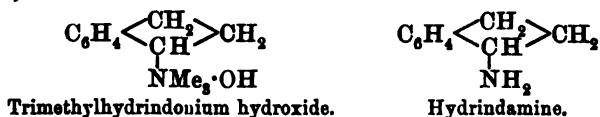
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XXVIII.—*Resolution of Trimethylhydrindonium Hydroxide into its Optically Active Components.*

By FREDERIC STANLEY KIPPING.

MANY attempts have already been made to resolve hydrindamine into its optically active components by fractionally crystallising its salts with optically active acids; the results of such experiments have shown that, in the case of some acids, *two* partially racemic hydrindamine salts are obtained in very unequal quantities (Trans., 1900, 77, 861; Kipping and Hall, Trans., 1901, 79, 430), whilst in that of others only one such partially racemic compound is formed (Trans., 1901, 79, 370; Kipping and Hall, *loc. cit.*, and Trans., 1901, 79, 446); in no case has it been found possible to obtain a salt which gives, on decomposition, an optically active base.

Under these circumstances, it appeared interesting to study the behaviour of externally compensated trimethylhydrindonium hydroxide (Kipping and Hall, Trans., 1900, 77, 469). This base contains an asymmetric carbon group very similar to that present in hydrindamine,



and might therefore be expected to show much the same behaviour as the latter towards a given optically active acid.

Experiments showed that this was not so; when trimethylhydrindonium bromocamphorsulphonate is submitted to fractional crystallisation, it does not yield two partially racemic salts corresponding with the hydrindamine bromocamphorsulphonates, but is gradually resolved into the salts of the enantiomorphously related bases; the salt of the dextrorotatory base which is finally isolated gives, on decomposition with potassium iodide, an optically active trimethylhydrindonium iodide. The behaviour of the quaternary base, therefore, is perfectly normal.

In attempting to account for the abnormal character of the hydrindamine salts, it was suggested that the observed isomerism might be conditioned by the configuration of the quinquivalent nitrogen atom. Now since the trimethylhydrindonium salts contain the group  $\text{-NMe}_3\text{X}$ , which, as regards any possible isomerism of this kind, would seem to be identical with the group  $\text{-NH}_2\text{X}$ , contained in the hydrindamine salts, it might be concluded that, on the resolution of the quaternary salt, such a view became untenable. This, however, is not a necessary or

even probable consequence of the new fact; the bromocamphorsulphate of the externally compensated quaternary base may consist of four isomerides corresponding with those which, it has been suggested, are formed from externally compensated hydrindamine and bromocamphorsulphonic acid, and the only difference in the two cases may be that in the former the four isomerides do not unite in pairs to give partially racemic salts; on fractional crystallisation, therefore, under the conditions employed, the most sparingly soluble salt is isolated, leaving a mixture which would contain three other isomerides. It would be useless at this stage to consider further the question of the isomerism of nitrogen compounds; experiments which are in progress may throw some light on the subject.

#### EXPERIMENTAL.

The racemic trimethylhydrindonium iodide (Kipping and Hall, *Trans.*, 1900, 77, 470) which was required for this work, was prepared by digesting an aqueous alcoholic solution of hydrindamine hydrochloride with methyl iodide and excess of potash until the solution no longer gave a vapour alkaline to litmus; on cooling, most of the product separated in pale yellow crystals, and the portion remaining in the mother liquors was obtained by evaporating to dryness with dilute hydrochloric acid, extracting the residue with boiling alcohol, and then concentrating the alcoholic extract.

*Trimethylhydrindonium Bromocamphorsulphonate,*  
 $C_{12}H_{18}NO \cdot SO_2 \cdot C_{10}H_{14}BrO$ .

On adding silver bromocamphorsulphonate, dissolved in aqueous alcohol, to a solution of trimethylhydrindonium iodide in the same solvent, a heavy precipitate of silver iodide is immediately formed; after heating together molecular proportions of the two compounds for about 30 minutes under these conditions to complete the interaction, the filtrate, on evaporation, yields an almost colourless syrup which soon begins to crystallise when kept over sulphuric acid.

The crude salt, when merely freed from oil with the aid of porous earthenware, consists of an ill-defined, crystalline mass, and has no definite melting point, liquefying gradually between about 155° and 165°; it is very readily soluble in water, alcohol, acetone, or chloroform, but only sparingly so in cold ethylic acetate. During damp weather, it liquefies or becomes pasty on exposure to the air.

In dilute aqueous solution, the salt gives the normal rotation, that is to say, its molecular rotation is the same as that of bromocamphorsulphonic acid.

0.25 gram dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha + 1^{\circ}6'$ ; hence  $[\alpha]_D + 55^{\circ}$  and  $[M]_D + 267^{\circ}$ .

A halogen determination was made with a sample dried over sulphuric acid :

0.2092 gave 0.0800 AgBr. Br = 16.3.

Calculated for  $C_{22}H_{32}NO_4BrS$ . Br = 16.5 per cent.

*Isolation of d-Trimethylhydrindonium Bromocamphorsulphonate.*—

The best way of carrying out the fractional crystallisation of the bromocamphorsulphonate is to dissolve the crude product in a small quantity of chloroform, and then heat on the water-bath until nearly all the chloroform has evaporated ; the salt is thus freed from traces of moisture and is left in the state of a syrup, which is mixed with a considerable volume of warm, dry ethyl acetate ; on cooling, crystallisation occurs and the salt separates in small, nodular aggregates or in the form of bulky masses of needles, the solution often setting to a paste which is difficult to filter. The deposit is separated, dissolved in dry chloroform, and the liquid treated as before. As these operations proceed, the melting point of the most sparingly soluble fraction gradually rises and becomes more sharply defined, until after some 10—20 crystallisations a uniform product, namely, *d*-trimethylhydrindonium *d*-bromocamphorsulphonate, is obtained. The rise in melting point is accompanied by an increase in the specific rotation of the most sparingly soluble fraction in aqueous solution ; thus after four operations, the specific rotation was  $[\alpha]_D + 60.5^{\circ}$  ; after ten,  $[\alpha]_D + 67.4^{\circ}$  ; after sixteen,  $[\alpha]_D + 71.3^{\circ}$ .

The mother liquors from the first operations give, on evaporation, deposits which can be easily crystallised from a mixture of chloroform and ethyl acetate, but the melting points of such deposits vary in a very irregular manner on recrystallisation, sometimes rising and sometimes falling ; for this reason, further attempts to isolate the bromocamphorsulphonate of the *l*-base were given up, and the mother liquors were directly employed for the preparation of the iodide of the *l*-base (p. 279).

*d*-Trimethylhydrindonium *d*-bromocamphorsulphonate is obtained in long, slender needles or prisms when its solution in chloroform and ethyl acetate is slowly evaporated ; it melts at 199—200°, decomposing a little. It is very readily soluble in water, acetone, alcohol, or chloroform, but almost insoluble in dry ether or ethyl acetate, even on boiling.

The specific rotation was determined in aqueous solution with three different preparations, of which II and III were successive crops of one sample.



I. 0.3445 gram dissolved in, and made up to 25 c.c. with, water, examined in a 200 mm. tube, gave  $\alpha + 1.97^\circ$ ; whence  $[\alpha]_D + 71.5^\circ$ .

II. 0.5088 gram under the same conditions;  $\alpha + 2.83^\circ$ ;  $[\alpha]_D + 69.5^\circ$ .

III. 0.5040 gram under the same conditions;  $\alpha + 2.78^\circ$ ;  $[\alpha]_D + 69.0^\circ$

The close agreement of the results obtained with II and III may be taken as evidence of the purity of the salt; the rather higher value of that obtained with I is possibly due to the solution being more dilute, determinations in alcoholic solution having shown that the specific rotation is considerably greater in the latter, less dissociating, solvent. That the salt is a pure substance is also shown by its behaviour on decomposition with potassium iodide.

Taking the mean of the above results, the molecular rotation of the salt is  $+340^\circ$ , and that of the acid ion being  $+270^\circ$ , the molecular rotation of the base ion would be  $+70^\circ$ ; this value agrees well with that calculated from the specific rotation of the iodide.

*d*-Trimethylhydrindonium Iodide,  $C_{12}H_{18}NI$ .

The iodide of the *d*-base is so much more readily soluble in water than that of the *dl*-base that it is not precipitated on mixing concentrated aqueous solutions of *d*-trimethylhydrindonium bromocamphorsulphonate and potassium iodide; it is best, therefore, to isolate the salt by evaporating the mixed solutions to dryness and extracting the powdered residue with boiling chloroform, in which the quaternary iodide is readily soluble.

It crystallises from water in long, highly lustrous, transparent needles, which, like the crystals of the racemic iodide, are anhydrous, but are quite different from the latter in crystallographic character, the racemic iodide forming compact, well-defined prisms. The salt of the active base decomposes at  $190$ — $191^\circ$ , giving, doubtless, indene and trimethylamine hydriodide (Kipping and Hall, *Trans.*, 1900, 77, 467); on heating the optically active and racemic iodide simultaneously, a difference in decomposing point of about  $5^\circ$  or  $6^\circ$  can be noticed, the racemic compound remaining unchanged until about  $197$ — $198^\circ$ . The active iodide is readily soluble in hot water, alcohol, or chloroform, but practically insoluble in ether or ethyl acetate.

That the salt just described, also the bromocamphorsulphonate of the *d*-base, are pure compounds, was proved by fractionally crystallising the iodide from warm water, and thus separating it into three portions; the whole was obtained in long needles, free from crystals of the racemic iodide, which if present could be easily recognised, as was proved by crystallising a mixture of the two salts.

As further proof of the purity of the iodide, the following determinations of the specific rotation of the first two fractions may serve:

I. 0.5333 gram dissolved in water and the solution diluted to 25 c.c. gave on examination in a 200 mm. tube  $\alpha + 0.92^\circ$ ; whence  $[\alpha]_D + 21.6^\circ$ .

II. 0.3949 gram under the same conditions:  $\alpha + 0.70^\circ$ ; whence  $[\alpha]_D + 22.2^\circ$ .

Taking the specific rotation to be  $+21.9^\circ$ , the molecular rotation is  $[M]_D + 66.3^\circ$ , a value which agrees well with that deduced from the molecular rotation of the bromocamphorsulphonate.

### *Picrates of the Externally Compensated and d-Bases.*

The picrates of the optically inactive and of the active bases are only very sparingly soluble in cold water and are easily obtained from the iodides by precipitation. The racemic picrate crystallises in compact, yellow prisms which melt and decompose at about  $188^\circ$ ; the active compound is more readily soluble in both water and alcohol, from which it separates in long, very slender needles melting at about  $167^\circ$ ; the differences between the picrates are therefore similar to those between the iodides.

### *l-Trimethylhydrindonium Iodide.*

As the deposits of trimethylhydrindonium bromocamphorsulphonate remaining after separating some of the salt of the *d*-base were found to behave as if they were complex mixtures, and it did not seem possible to separate from them any other salt, the last mother liquors were evaporated and the residue treated with potassium iodide as already described; after separating the racemic iodide, which was precipitated in large quantities, the mother liquors were evaporated to dryness and extracted with boiling chloroform. In this way, a salt, obviously the iodide of the *l*-base, was isolated without difficulty; it crystallised from water in large, fern-like masses, and its aqueous solution was laevorotatory.

The author's thanks are due to Mr. L. L. Lloyd for assistance in preparing some of the materials for this investigation.

Part of the expense incurred in carrying out this work was met by a grant from the Government Grant Fund of the Royal Society, for which the author desires to express his thanks.

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XXIX.—*The Action of Methylene Diiodide on Aryl- and Naphthyl-amines: Diarylmethylenediamines, Acridines, and Naphthacridines.*

By ALFRED SENIER and WILLIAM GOODWIN.

In a recent paper (Trans., 1901, 79, 254), we described two ethylene-diaryldiamines which resulted from the interaction of ethylene dibromide and xylydine and  $\psi$ -cumidine respectively. At the same time, we mentioned that we had extended the reaction to the methylene series and had obtained well crystallisable compounds. Methylene diiodide was found to give better results than either the dibromide or dichloride. We now submit the results of further study of those compounds and of the reaction generally. It was expected that these derivatives would prove to be methylenediamines or, at least, to belong to one of the classes of compounds which are known to result from the action of ethylenedibromide on aniline. They might, for example, be methylenediamines,  $\text{CH}_2(\text{NHR}')_2$ , methyleneaniline homologues,  $\text{CH}_2\text{:NR}'$ , methylenepiperazines,  $\text{CH}_2\left\langle \begin{smallmatrix} \text{NR}' \\ \text{NR}' \end{smallmatrix} \right\rangle \text{CH}_2$ , or

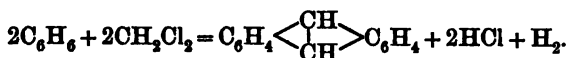
higher polymerides,  $\begin{smallmatrix} \text{CH}_2\text{:NR}'\text{:CH}_2 \\ \text{NR}'\text{:CH}_2\text{:NR}' \end{smallmatrix}$ . This view is in agreement with that of previous inquirers (Lermontoff, *Ber.*, 1874, 7, 1252; Grünhagen, *Annalen*, 1890, 256, 219 and 285; Bischoff and Nastvogel, *Ber.*, 1890, 23, 2055).

Parallel with the reaction of arylamines and methylene diiodide is the corresponding reaction between arylamines and formaldehyde or methylene oxide,  $\text{CH}_2\text{:O}$ . The experiments of Pratesi (*Gazzetta*, 1884, 14, 351), Tollens (*Ber.*, 1884, 17, 653), Wellington and Tollens (*Ber.*, 1885, 18, 3298), Eberhardt and Welter (*Ber.*, 1894, 27, 1804), and Grassi-Cristaldi and Schiavo-Leni (*Gazzetta*, 1900, 30, ii, 112) with this latter reaction led to the discovery of the diamines and isomeric methylenearylamines previously referred to. The diamines were also shown to give rise by metastatic change to a series of methylene benzidenes. Methylenediphenyldiamine,  $\text{CH}_2(\text{NHPh})_2$ , for example, giving diaminodiphenylmethane,  $\text{CH}_2(\text{C}_6\text{H}_4\text{NH}_2)_2$ .

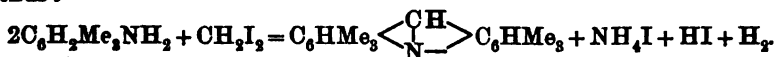
The study of these reactions by the investigators mentioned, evidently conducted with the greatest care, has led to very contradictory results. The physical characters of the compounds described under the same name differ enormously, and the analytical data are far from satisfactory (compare Bischoff and Nastvogel). Working with aniline and the toluidines, our experience has been the same. This is due, no doubt, partly to the proved instability of the compounds

formed, and partly to their number and the difficulty of separating them. With the increase in the number of alkyl groups, as in the case of xylidine and  $\psi$ -cumidine, the reaction becomes more definite, and with methylene di-iodide assumes a new character. With  $\psi$ -cumidine, beautiful, yellow crystals are obtained, easily recrystallised or sublimed, and in this way readily obtained of a constant and definite melting point. Elementary analysis proved that it was not a member of any of the classes of compounds alluded to above. It gave C = 86.8, H = 8.41, N = 5.42 per cent., whereas methylenedicyumyldiamine or its isomerides would require C = 80.85, H = 9.22, N = 9.93 per cent., and methylenecumidine or its isomerides would require C = 81.63, H = 8.84, N = 9.52 per cent. The relative proportion of nitrogen found pointed to a condensation reaction whereby ammonia or a derivative was evolved. This view found confirmation in the fact that the odour of ammonia was observed during the course of the reaction, and also that a notable quantity of ammonium iodide collected in the tube of the reflux condenser employed in the experiment. The solutions of the compound exhibited a marked and very beautiful fluorescence, and this, together with the high melting point, 221—222°, also indicated condensation.

Consideration of the paper by Friedel and Crafts (*Ann. Chim. Phys.*, 1887, [vi], 11, 263) led to the hypothesis that the compound was an anthramine from which an amino-group had split off. These investigators found that benzene and methylene dichloride condensed to anthracene in presence of aluminium chloride thus :



The hydrogen formed, acting on an excess of methylene dichloride, gave, by a secondary reaction, methyl chloride. To make certain of the right conditions, we repeated this experiment and obtained anthracene. Cumidine was substituted for benzene and the experiment repeated, but no reaction appeared to take place, and when methylene diiodide replaced the dichloride in the last experiment, the yellow, crystalline compound was obtained, but only to the same extent as in the absence of the aluminium chloride. We next modified the hypothesis by supposing condensation to take place at the position of the liberated nitrogen group. In this way, an acridine might be formed, thus :



The odour of methyl iodide was always noticed, which would explain what becomes of the hydrogen written as free in the equation as in the reaction of Friedel and Crafts. Such a hexamethylacridine would

require C = 86.61, H = 8.06, N = 5.33 per cent., which is in agreement with the experimental numbers. A vapour density determination, using boiling sulphur, was found to be possible by Victor Meyer's method :

0.1303 gave 11.8 c.c. at 18° and 767.5 mm. Density = 130.

$C_{10}H_{21}N$  requires density = 131.5.

Further evidence in favour of this view was found in the experiments of Bernthsen and Bender (*Ber.*, 1883, 16, 1802), who prepared acridine from diphenylamine and formic acid, for dicumylamine might well result from cumidine and hydriodic acid, and formic acid is hydroxymethylene oxide. Similar analogies were found in the work of Möhlau (*Ber.*, 1886, 19, 2451).

Any doubt, however, that might remain as to the  $\psi$ -cumidine compound being hexamethylacridine was set at rest by the extension of the reaction to the  $\alpha$ - and  $\beta$ -naphthylamines. These bases were found to react with methylene diiodide in precisely the same manner as  $\psi$ -cumidine. The same odour of ammonia and of methyl iodide was noticed, and the same condensation of ammonium iodide in the reflux condenser tube. From each of the naphthylamines we obtained yellow crystals with well-defined melting points, and their solutions exhibited the characteristic, well-marked fluorescence. On analysis, the numbers obtained agreed with those of naphthacridine. Finally, the  $\beta$ -compound was identified by its melting point and other characters with  $\beta$ -naphthacridine discovered by Reed (*J. pr. Chem.*, [ii], 1886, 34, 160; 1887, 35, 298) as a result of the action of methylal or of formaldehyde on  $\beta$ -naphthylamine. This base has also been studied in an interesting paper by Morgan (*Trans.*, 1898, 73, 536). In a preliminary communication (*Proc.*, 1898, 14, 132), Morgan announced that the result of experiments on  $\alpha$ -naphthylamine would be published later. Meanwhile, we have obtained  $\alpha$ -naphthacridine by the methylene diiodide reaction.

We find, then, that methylene diiodide yields methylene diamines with aniline, as originally stated by Lermontoff, also with xyloidine and probably with the three toluidines. With  $\psi$ -cumidine, however, and with both  $\alpha$ - and  $\beta$ -naphthylamines, condensation takes place with the formation of acridines. The acridines do not react with phenyl carbimide forming ureas, but the methylenediamines do so in the same manner as their ethylene homologues (*Trans.*, 1901, 79, 258), at least so far as we have been able to complete their investigation.

The further study of  $\alpha$ -naphthacridine and of hexamethylacridine we desire to reserve for another communication.

*Diarylmethylenediamines.**Diphenylmethylenediamine*,  $\text{CH}_2(\text{NHPb})_2$ .

Methylene diiodide and aniline, in equal molecular proportions, were brought together with an excess of dry potassium carbonate in a flask fitted with a reflux condenser. The flask was placed in a paraffin-bath which was heated gradually to about  $150^\circ$ , when a violent reaction soon took place. The flask was then removed from the bath until this moderated, when it was replaced and the heating continued for 4 hours. After cooling, the residue in the flask was treated with hot water to remove potassium salts. The dark red, semi-solid mass remaining was freed from aniline by distillation with steam. The resulting mass solidified on cooling, and, when reduced to powder, was of a dark yellow colour. It melted at  $65\text{--}67^\circ$ . After boiling with alcohol, the melting point rose to  $140^\circ$ . Diphenylmethylenediamine, described by Eberhardt and Welter, melted at  $64\text{--}65^\circ$ , and by boiling with alcohol it was changed into methyleneaniline which melts at  $139^\circ$ . On analysis:

0.2502 gave 0.7148  $\text{CO}_2$  and 0.1590  $\text{H}_2\text{O}$ . C = 77.92; H = 7.06.

$\text{C}_{13}\text{H}_{14}\text{N}_2$  requires C = 78.75; H = 7.07 per cent.

*Diphenylmethylenediamine Platinichloride*,  $\text{CH}_2(\text{NHPb})_2, \text{H}_2\text{PtCl}_6$ , separated as an olive-green precipitate on the addition of a solution of platinic chloride to the base dissolved in dilute hydrochloric acid. The salt was washed with water and dried in a vacuum over sulphuric acid. On analysis:

0.2318 gave 0.0736 Pt. Pt = 31.75.

$\text{C}_{13}\text{H}_{14}\text{N}_2, \text{H}_2\text{PtCl}_6$  requires Pt = 32.06 per cent.

*Dicarbonyldiphenylmethylenediamine*,  $\text{CH}_2(\text{NPh}\cdot\text{CO}\cdot\text{NHPb})_2$ , was obtained by treating the base with phenylcarbimide in the manner described by us (Trans., 1901, 79, 258). The closed tube was heated at  $120\text{--}124^\circ$  for 3 to 4 hours. The residue was washed with dry ether and recrystallised from glacial acetic acid. The melting point is not definite. On analysis:

0.2750 gave 0.7397  $\text{CO}_2$  and 0.1668  $\text{H}_2\text{O}$ . C = 73.35; H = 6.74.

$\text{C}_{27}\text{H}_{24}\text{N}_4\text{O}_2$  requires C = 74.31; H = 5.50 per cent.

*Diethylmethylenediamines*,  $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$ .

Methylene diiodide (1 mol.) with toluidine (2 mols.), together with potassium carbonate, were heated in the manner described for the phenyl-homologue and the subsequent procedure was the same, except that the distillation with steam was omitted. The *o*-tolyl derivative,

probably di-*o*-tolylmethylenediamine, crystallised from alcohol in large, colourless, foliate crystals. After repeated recrystallisation, these melted at 156—157°. On analysis:

0.2888 gave 0.8374 CO<sub>2</sub> and 0.2124 H<sub>2</sub>O. C = 79.08; H = 8.17.

0.3550 „ 38 c.c. moist nitrogen at 16° and 756.5 mm. N = 12.41.

C<sub>15</sub>H<sub>18</sub>N<sub>2</sub> requires C = 79.64; H = 7.96; N = 12.39 per cent.

From *o*-toluidine and methylene chloride, Grünhagen obtained two bases; one was a liquid and the other melted at 135°. Using formaldehyde, Eberhardt and Welter prepared a base which melted at 52°. The *p*-tolyl derivative, probably di-*p*-tolylmethylenediamine, was obtained in small, pale yellow crystals from solution in a mixture of alcohol and chloroform. After several recrystallisations, it melted at 149—150°. On analysis:

0.2562 gave 0.7456 CO<sub>2</sub> and 0.1800 H<sub>2</sub>O. C = 79.37; H = 7.8.

0.1630 „ 0.4776 CO<sub>2</sub> „ 0.1168 H<sub>2</sub>O. C = 79.91; H = 7.96.

C<sub>15</sub>H<sub>18</sub>N<sub>2</sub> requires C = 79.64; H = 7.96 per cent.

We were not successful in isolating a *m*-tolyl derivative in a definite form. Yellow, amorphous compounds were obtained in two experiments. The one melted at 78°, the other at 160°.

*Dixylylmethylenediamine*, CH<sub>2</sub>(NH·C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>)<sub>2</sub>.

Methylene diiodide (1 mol.) and xylidine (2 mols.) were treated in the same manner as in the corresponding reaction with the toluidines. The base, recrystallised several times from rectified spirit, consisted of pale yellow, large, foliate crystals, and melted at 127—128°. On analysis:

0.2592 gave 0.7576 CO<sub>2</sub> and 0.2140 H<sub>2</sub>O. C = 79.71; H = 9.17.

0.3743 „ 35.2 c.c. moist nitrogen at 13° and 767 mm. N = 11.21.

C<sub>17</sub>H<sub>22</sub>N<sub>2</sub> requires C = 80.31; H = 8.67; N = 11.02 per cent.

*Dixylylmethylenediamine Platinichloride*,



was precipitated when an alcoholic solution of platinic chloride was added to an alcoholic solution of the base acidified with hydrochloric acid. The precipitate, of a golden-yellow colour, was dried at 100°. On analysis:

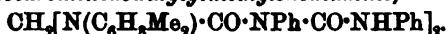
0.2076 gave 0.0620 Pt. Pt = 29.86.

C<sub>17</sub>H<sub>22</sub>N<sub>2</sub> requires Pt = 29.36 per cent.

*Nitro*-derivatives of dixylylmethylenediamine are produced readily by direct nitration. Two experiments were made, but the products were evidently mixtures. One contained N = 11.5 and the other

N = 12·7 per cent. A mononitro-derivative requires N = 9·82 and a dinitro- N = 16·28 per cent.

*Dicarbaniilidocarbaniilidodixylylmethylenediamine,*



—When an excess of phenylcarbimide reacts with dixylylmethylenediamine, a urea derivative is formed from 4 molecules of the carbimide instead of 2 molecules, as in other cases. The reaction described (Trans., 1901, 79, 258) may be supposed to occur twice in each amino-group of the diamine. This reaction is, indeed, only an extension of Wöhler's urea synthesis, for it may be assumed that a methylenediammonium dicyanate is first formed, which metastasises to urea. An excess of phenyl carbimide was heated in a closed tube with the base at 150° for 6 hours; the contents of the tube, freed from excess of phenylcarbimide by evaporation, consisted of a yellowish-white substance resembling in appearance imperfectly bleached beeswax, this was washed with dry ether, which effected no apparent change. When rubbed in a mortar with successive small quantities of alcohol, there was left a hard, white residue, which was dissolved in more alcohol, and was recrystallised several times from that medium. Well-formed, colourless needles were thus obtained which melt at 203°. On analysis:

0·2766 gave 0·7438 CO<sub>2</sub> and 0·1470 H<sub>2</sub>O. C = 73·33; H = 5·9.

0·2978 „ 28·1 c.c. moist nitrogen at 10° and 754 mm. N = 11·21.

C<sub>45</sub>H<sub>42</sub>N<sub>6</sub>O<sub>4</sub> requires C = 73·97; H = 5·75; N = 11·5 per cent.



The constitution of this hexamethylacridine we reserve for further investigation. If, however, it be supposed that the positions of condensation are neighbouring to the amino-groups, the positions of the methyl groups are 1 : 2 : 4 and 5 : 6 : 8. *ψ*-Cumidine, which melted at 67° (2 mols.), with methylene diiodide (1 mol.), and an excess of potassium carbonate were taken. The cumidine and potassium carbonate were melted together and then brought into a flask fitted with a reflux condenser, to which the weighed amount of methylene diiodide was then added; the flask and its contents were heated in a paraffin bath until a temperature of about 160° was reached, when an energetic reaction took place; the flask was removed from the bath until the violence had subsided, when it was replaced and the temperature continued at 150—160° for about 6 hours. The formation of a sublimate in the tube of the condenser continued during the course of the reaction, and its ceasing to form was an indication that the heating had been sufficiently prolonged. This method was found to give better



results than when the diiodide was added in small quantities at a time. No advantage, either, was found in omitting the alkali and treating the product afterwards with potassium hydroxide. The contents of the flask were then treated with hot water to remove potassium salts, when there remained a yellow, crystalline mass; after being washed with dilute alcohol, this assumed a greenish-yellow colour. It was next dissolved and recrystallised from alcohol or, in some cases, from acetone or light petroleum, when extremely fine, yellow crystals, usually needles, were obtained. These crystals are slightly soluble in alcohol or ether and more soluble in acetone, chloroform, benzene, or light petroleum. They are insoluble in water. All the solutions exhibit a beautiful, green fluorescence. Purified by repeated recrystallisation or sublimation, the compound melts at  $221-222^\circ$ , and sublimes easily without decomposition. On analysis:

0.2406 gave 0.7658  $\text{CO}_2$  and 0.1823  $\text{H}_2\text{O}$ .  $\text{C} = 86.80$ ;  $\text{H} = 8.41$ .

0.2622 „ 0.8290  $\text{CO}_2$  „ 0.1992  $\text{H}_2\text{O}$ .  $\text{C} = 86.23$ ;  $\text{H} = 8.44$ .

0.2454 „ 0.7756  $\text{CO}_2$  „ 0.1770  $\text{H}_2\text{O}$ .  $\text{C} = 86.20$ ;  $\text{H} = 8.01$ .

0.3430 „ 16 c.c. moist nitrogen at  $15^\circ$  and 755.5 mm.  $\text{N} = 5.42$ .

$\text{C}_{10}\text{H}_{21}\text{N}$  requires  $\text{C} = 86.69$ ;  $\text{H} = 7.98$ ;  $\text{N} = 5.32$  per cent.

Using methylene dibromide instead of diiodide, the acridine was obtained, but the yield was much less. With methylene dichloride, no acridine was formed. In the latter experiment, a marked odour of an isonitrile was noticed.

*Hexamethylacridine Picrate*,  $\text{C}_6\text{HMe}_3 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{HMe}_3 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$ , was prepared by adding an alcoholic solution of picric acid to an alcoholic solution of the base, heating to boiling, and allowing to stand. Very fine, brown, plume-like crystals separated. These were collected on a filter and washed with a small quantity of alcohol and again with dilute alcohol and dried at  $110^\circ$ . They melted, not very sharply, at  $200-202^\circ$ . On analysis:

0.3090 gave 30.5 c.c. moist nitrogen at  $18^\circ$  and 752.5 mm.  $\text{N} = 11.27$ .

$\text{C}_{19}\text{H}_{21}\text{N} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$  requires  $\text{N} = 11.38$  per cent.

*Dinitrohexamethylacridine*,  $\text{C}_6(\text{NO}_2)_2\text{Me}_3 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6(\text{NO}_2)_2\text{Me}_3$ , was produced by treating the base with concentrated nitric acid, boiling well, and pouring the solution into water; the yellow precipitate was collected on a filter, well washed with water and dried on a porous plate. It melted at  $85-87^\circ$ . It was dried in an exhausted desiccator over sulphuric acid, and on analysis:

0.2064 gave 20.3 c.c. moist nitrogen at  $18^\circ$  and 761 mm.  $\text{N} = 11.37$ .

$\text{C}_{16}\text{H}_{10}(\text{NO}_2)_2\text{N}$  requires  $\text{N} = 11.89$  per cent.

*Tribromohexamethylacridine*,  $C_6BrMe_3 \begin{smallmatrix} \text{CBr} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_6BrMe_3$ , was obtained

by exposing the base to the action of bromine vapour for 3 days in a covered vessel. The product was heated on a water-bath to remove excess of bromine and then allowed to stand in a desiccator over solid potassium hydroxide for 2 days. Finally, the red compound was heated in an air-bath at  $105^\circ$ . On analysis by Carius's method:

0.3116 gave 0.3466 AgBr. Br = 47.33.

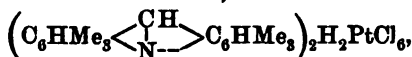
$C_{19}H_{18}Br_3N$  requires Br = 47.98 per cent.

*Hexamethylacridine Nitrate*,  $C_6HMe_3 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_6HMe_3 \cdot HNO_3$ , was formed by adding dilute nitric acid to an alcoholic solution of the base, warming for a short time on a water-bath, and then setting aside to crystallise. On standing, the solution, which had a deep orange colour, deposited bright scarlet needles. An attempt was made to further purify the compound by recrystallisation from dilute alcohol, but this treatment was found to decompose the salt regenerating the original base. The needles were washed with a little alcohol only and partly dried by pressing between filter-paper. Finally, they were dried at  $100^\circ$  and left over sulphuric acid in a desiccator. They melted with decomposition at  $163\text{--}164^\circ$ . On analysis:

0.3356 gave 25.1 c.c. moist nitrogen at  $14^\circ$  and 770 mm. N = 8.92.

$C_{19}H_{21}N \cdot HNO_3$  requires N = 8.59 per cent.

*Hexamethylacridine Platinichloride*,



separated in the form of scarlet needles on the addition of a solution of platinic chloride to a solution of the base in dilute hydrochloric acid. Like acridine salts generally, it is decomposed by treatment with water or boiling with alcohol. On analysis:

0.0577 gave 0.0118 Pt. Pt = 20.45.

$(C_{19}H_{21}N)_2 \cdot H_2PtCl_6$  requires Pt = 20.82 per cent.

*Hexamethylacridine Aurichloride*,  $C_6HMe_3 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_6HMe_3 \cdot HAuCl_4$ ,

was obtained in a similar manner to the platinichloride. It is yellow, and on analysis:

0.1110 gave 0.0358 Au. Au = 32.25.

$(C_{19}H_{21}N) \cdot HAuCl_4$  requires Au = 32.70 per cent.

*Hexamethylacridine Mercurichloride*,  $C_6HMe_3 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_6HMe_3 \cdot HgCl_2$ .

—An alcoholic solution of the base acidified with hydrochloric acid was

mixed with an alcoholic solution of mercuric chloride and the mixture allowed to stand. Dark red, glistening needles with a characteristic yellow lustre separated. On analysis:

0.3076 gave 0.1272 HgS.  $Hg = 35.65$ .

$(C_{10}H_{21}N)HgCl_2$  requires  $Hg = 35.11$  per cent.

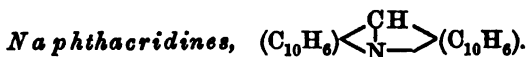
*Hexamethylacridine Dichromate*,  $C_6HMe_3 \begin{smallmatrix} CH \\ | \\ N \end{smallmatrix} C_6HMe_3 \cdot H_2Cr_2O_7$ , was formed on the addition of a solution of potassium dichromate to a solution of the base in hydrochloric acid. It consists of deep red crystals which were washed rapidly and dried at  $100^\circ$ . On analysis:

0.6536 gave 0.1378  $Cr_2O_3$ .  $Cr = 14.44$ .

$(C_{10}H_{21}N)H_2Cr_2O_7$  requires  $Cr = 14.00$  per cent.

Other salts examined were the *sulphate*, forming dark red crystals, which do not melt below  $285^\circ$ ; the *hydrochloride*, red crystals which decompose on heating, and the *nitrite*, a pale yellow powder obtained by adding potassium nitrite to a solution of the base in glacial acetic acid. The nitrite decomposes on heating.

An *ethylhexamethylacridinium iodide* was also prepared but not further examined. The base was heated with excess of ethyl iodide in a closed tube for 4 hours. It consists of bronze-coloured crystals which, after drying on a porous plate, melted at  $214-215^\circ$ .



*$\alpha$ -Naphthacridine.*

$\alpha$ -Naphthylamine (2 mols.), methylene diiodide (1 mol.), and an excess of potassium carbonate were treated exactly as in the case of the corresponding cumidine experiment. The contents of the flask were washed with water, then with a small proportion of alcohol, after which the residue was dissolved in and recrystallised from alcohol. More than one compound appeared to be formed, and the acridine was best separated by sublimation and subsequent recrystallisation from alcohol. It consists of pale yellow crystals which melt at  $173^\circ$ . The colour becomes darker on exposure to light. It is soluble in chloroform, ether, acetone, benzene, or light petroleum. The fluorescence exhibited by its solutions is very noticeable. In solution in benzene, it is red-green, in the other solvents it is violet or blue. On analysis:

0.1532 gave 0.5040  $CO_2$  and 0.0707  $H_2O$ .  $C = 89.72$ ;  $H = 5.12$ .

0.1783 „ 7.6 c.c. moist nitrogen at  $9^\circ$  and 764 mm.  $N = 5.15$ .

$C_{21}H_{13}N$  requires  $C = 90.32$ ;  $H = 4.66$ ;  $N = 5.02$  per cent.

The following are the only derivatives obtained so far, but the work is being continued.

*Mononitro- $\alpha$ -naphthacridine*,  $C_{21}H_{13}(NO_2)N$ , was precipitated when the base was warmed with concentrated nitric acid and the mixture thrown into water. After washing and drying, first on a porous plate and then in an exhausted desiccator over sulphuric acid, it melted at  $105-107^\circ$ . On analysis :

0.3248 gave 24.8 c.c. moist nitrogen at  $16^\circ$  and 767.5 mm.  $N = 8.85$ .

$C_{21}H_{13}(NO_2)N$  requires  $N = 8.64$  per cent.

A second nitro-derivative was prepared which, after recrystallisation from alcohol and drying, melted at  $185^\circ$ , but was not further examined.

( $\alpha$ )-*Naphthacridine Platinichloride*,  $C_{10}H_6 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_{10}H_6, H_2PtCl_6, 2H_2O$ , was obtained in the form of small, deep yellow crystals on allowing a mixture of alcoholic solutions of the base and platinic chloride, acidulated with hydrochloric acid, to stand. They could not be subjected to  $100^\circ$  without decomposition. Dried over sulphuric acid and analysed :

0.1676 gave 0.0322 Pt.  $Pt = 19.2$ .

$(C_{21}H_{13}N)_2, H_2PtCl_6, 2H_2O$  requires  $Pt = 19.41$  per cent.

*$\alpha$ -Naphthacridine Picrate*,  $C_{10}H_6 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_{10}H_6, C_6H_3(NO_2)_3 \cdot OH$ , was formed by mixing alcoholic solutions of the base and picric acid. It separated in the form of scarlet needles. These were washed with a little alcohol and dried by pressing between filter paper, and afterwards by leaving them in an exhausted desiccator over sulphuric acid. It melts at  $176-178^\circ$ . On analysis :

0.2312 gave 21 c.c. moist nitrogen at  $10^\circ$  and 771.5 mm.  $N = 11.03$ .

$C_{21}H_{13}N, C_6H_3(NO_2)_3OH$  requires  $N = 11.02$  per cent.

### *$\beta$ -Naphthacridine.*

The process adopted for the preparation of  $\alpha$ -naphthacridine yields its  $\beta$ -isomeride with greater readiness and in better yield. After sublimation and recrystallisation from alcohol, it consists of pale yellow needles which darken on exposure to light. It melts at  $215.5^\circ$ . It is soluble in chloroform, ether, benzene, or light petroleum, and sparingly so in alcohol; the solutions exhibit the characteristic blue fluorescence. On analysis :

0.1882 gave 0.6172  $CO_2$  and 0.0858  $H_2O$ .  $C = 89.44$  ;  $H = 5.06$ .

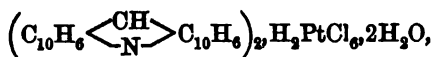
0.1990 „ 0.6540  $CO_2$  „ 0.0916  $H_2O$ .  $C = 89.63$  ;  $H = 5.11$ .

0.4260 „ 17.8 c.c. moist nitrogen at  $13^\circ$  and 776 mm.  $N = 5.05$ .

$C_{21}H_{13}N$  requires  $C = 90.32$  ;  $H = 4.66$  ;  $N = 5.02$  per cent.

The compound is identical with the  $\beta$ -naphthacridine discovered by Reed, who gives its melting point as  $216^\circ$ . We obtained the following derivative, which has not been previously described.

*β-Naphthacridine Platinichloride,*



precipitated as a golden-yellow powder on the addition of alcoholic solution of platinic chloride to an alcoholic solution of the base acidified with hydrochloric acid. Dried over sulphuric acid and analysed:

0.1396 gave 0.027 Pt. Pt = 19.34.

$(\text{C}_{21}\text{H}_{18}\text{N})_3 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$  requires Pt = 19.41 per cent.

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### XXX.—*The Polymerisation of Cyanic Acid: Cyanuric Acid, and Cyamelide.*

By ALFRED SENIER and THOMAS WALSH.

WHEN liquid cyanic acid is allowed to polymerise at 0°, or just above that temperature, it changes, as is well known, into a snow-white solid, the "insoluble cyanuric acid" or cyamelide of Liebig and Wöhler (*Ann. Phys. Chem.*, 1830, 20, 384). This solid is not, however, cyamelide only, as is generally supposed, but a mixture of the two isomerides, cyamelide and cyanuric acid. The two compounds are readily separated by treatment with water, in which cyamelide is very sparingly soluble. Having prepared, in this way, cyamelide in a state of purity not hitherto described, we made determinations of its solubility and compared it with the solubility of cyanuric acid. We also made numerous attempts to cause it to enter into reaction with other compounds. The results, although negative, are in some instances interesting as bearing on the theory of its constitution.

*Polymerisation of Cyanic Acid.*—The liquid cyanic acid employed was prepared by distilling dry cyanuric acid in an apparatus made of hard glass tubing similar to that used by von Baeyer (*Annalen*, 1860, 114, 165). The horizontal sealed end of the tube containing the cyanuric acid was heated in a short Hofmann combustion furnace, and so arranged that the bend leading to the U-shaped condenser portion was kept hot by the furnace. The condenser was kept at a temperature a few degrees below 0°. Liquid cyanuric acid, which was always slightly turbid, collected. When the temperature was allowed to rise to 0°, the liquid changed into a white solid. The polymerisation became violent and was accompanied by loud reports when a higher temperature was employed. 0.839 gram of this white solid, which had been

obtained from some cyanic acid almost free from turbidity, was finely powdered and treated with excess of hot water. The insoluble residue, after drying, weighed 0.253 gram and was about 30 per cent. of the substance taken. The washings on evaporation yielded crystals of cyanuric acid which gave the characteristic pink ammonio-cupric salt of Wöhler.

*Solubility of Cyamelide and of Cyanuric Acid.*—Some of the less soluble portions of the mixed polymerides were placed in a wash-bottle made of a large test-tube; boiling water was added and the contents were agitated for 2 hours by a current of air; the apparatus was then placed for 12 hours in water kept at about 15°; afterwards the contents were again agitated for an hour and the proportion of solid in solution was determined. As the result of numerous experiments, it was found that the percentage of solid dissolved decreased after each successive treatment with water in the case of every specimen examined, until it attained to from 0.008 to 0.01 per cent., when it became constant. The residues from the washings until the solubilities mentioned were attained responded in all cases to Wöhler's test for cyanuric acid, but after that point was reached the residues ceased to give that reaction. The solubility of cyamelide in water may therefore be taken as 0.01 per cent. at 15°. Determined in the same manner, as the result of very many experiments, we find the solubility of cyanuric acid to be from 0.145 to 0.160 per cent. at 15° (compare Lemoult, *Compt. rend.*, 1895, 121, 351). A specimen of cyamelide having the solubility mentioned was submitted to elementary analysis:

0.2762 gave 0.2845 CO<sub>2</sub> and 0.0678 H<sub>2</sub>O. C = 28.09; H = 2.72.  
(CONH)<sub>3</sub> requires C = 27.9; H = 2.32 per cent.

*Further Experiments with Cyamelide.*—Cyamelide was treated with phosphorus pentachloride, but without any change occurring. Cyanuric acid yields, under the same circumstances, cyanuric chloride, and this was verified by an experiment. It was suggested by Klason (*J. pr. Chem.*, 1885, [ii], 33, 129) that cyamelide is isocyanuric acid related to the isocyanuric esters, just as cyanuric acid is related to the normal cyanuric esters. It is interesting, therefore, as evidence of this view that as the normal esters and normal cyanuric acid yield a chloride with phosphorus pentachloride, so the *iso*-esters, and now it is proved cyamelide, do not do so.

Attempts were made to prepare silver, bromine, and other derivatives, but they were not successful.

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# XXXI.—*Magnetic Rotation of Ring Compounds. Camphor, Limonene, Carvene, Pinene, and some of their Derivatives.*

By W. H. PERKIN, sen., Ph.D., F.R.S.

DURING the course of my experiments on the magnetic rotation of substances belonging to the aliphatic and aromatic series, very remarkable differences have been observed in the values obtained for the two series of compounds, but there is a class of substances which are, in a sense, intermediate between the two series, namely, saturated closed chain compounds, such as the derivatives of tri-, tetra-, penta-, and hexa-methylene; these have also received a certain amount of attention, but unfortunately the number of such compounds available has been small. A comparison of the results obtained in the examination of the latter with those of the aliphatic and aromatic series led me to include in my investigations some of the members of the camphor and terpene series and their derivatives, not only on account of the great interest which always attaches to these important products, but also on account of their relationship to the saturated closed chain compounds mentioned above.

In previous papers on the magnetic rotation of substances belonging to the aliphatic series, it has been repeatedly pointed out that unsaturated members of this series differ from the corresponding saturated compounds by a number which varies between 0·7 and about 1·112, according to the class of compound. This will be seen from the following table :

			Diff. for unsaturation.
Octylene .....	$\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_4 \cdot \text{CH}_3 \dots$	9·435	} + 0·743
Octane .....	$\text{CH}_3 \cdot [\text{CH}_2]_6 \cdot \text{CH}_3 \dots$	8·692	
Allylacetic acid ...	$\text{CH}_2 : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \dots$	6·426	} + 0·913
Valeric acid .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \dots$	5·513	
Allyl alcohol .....	$\text{CH}_2 : \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \dots$	4·682	} + 0·914
Propyl alcohol ...	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \dots$	3·768	
Ethyl crotonate...	$\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{C}_2\text{H}_5 \dots$	7·589	} + 1·112
Ethyl butyrate ...	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{C}_2\text{H}_5 \dots$	6·477	

In the case of the hydrocarbons, the value for unsaturation is the lowest, and the average for all the hydrocarbons of this class which have been examined is 0·720 (Trans., 1895, 67, 261), whilst the highest number is obtained in the case of the carboxylic esters, and is, on the average, 1·112.

That this large *plus* difference is due to the formation, from the

*saturated aliphatic* substance, of a new class which we call *unsaturated*, and not merely to the removal of two atoms of hydrogen, is obvious, since the value of two hydrogen atoms has been shown to be +0.508, and their removal would therefore *reduce* the rotation.

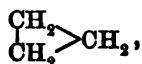
The next point to be considered is that closed carbon chains have a lower rotation than the corresponding open chain compounds, from which they differ by two atoms of hydrogen. This will be clear from a comparison of the magnetic rotation values of certain closed chain compounds with those of the corresponding open chain aliphatic compounds containing two atoms of hydrogen more :

Butyric acid .....	$C_4H_8O_2$ ...	4.472	} - 0.331
Trimethylenecarboxylic acid* .....	$C_4H_6O_2$ ...	4.141	
Valeric acid .....	$C_5H_{10}O_2$ ...	5.513	} - 0.465
Tetramethylenecarboxylic acid† .....	$C_5H_8O_2$ ...	5.048	
Hexoic acid .....	$C_6H_{12}O_2$ ...	6.530	} - 0.639
Pentamethylenecarboxylic acid‡ .....	$C_6H_{10}O_2$ ...	5.891	
Octoic acid .....	$C_8H_{16}O_2$ ...	8.580	} - 0.605
Methylhexamethylenecarboxylic acid§	$C_8H_{14}O_2$ ...	7.975	

In this connection, it will be convenient to consider the irregularities of these differences, which in the above table vary from about 0.33—0.64. This peculiarity has hitherto been an enigma, but careful study of the subject seems to show that this apparent anomalous behaviour is due to the comparison having been made between wrong members of the two series.

The study of the magnetic rotation of the aliphatic compounds has shown that the first two members of a series do not follow the same rule as the succeeding ones. In the carboxylic acids, for instance, formic acid yields a rotation very much higher, relatively, than any other acid. The value for acetic acid is also, relatively, too high, but to a less extent, whilst all the other acids differ by a constant value, as is seen in the diagram published in an earlier paper (Trans., 1884, 45, 548).

Now it is evident that the trimethylene ring,



must be the first member of the series of ring compounds, the tetra-,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , the second, and the penta-,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , the third, and so on, and it will be found, if these be compared with the first, second, and third members of the corresponding saturated aliphatic series, and

\* Trans., 1895, 67, 117.

† Trans., 1894, 65, 99.

‡ Trans., 1887, 51, 11.

§ Trans., 1888, 53, 209.



the usual allowance be made for additions of  $\text{CH}_2$  groups, that these anomalies in the value of ring formation due to loss of  $\text{H}_2$ , practically vanish, thus :

	Mol. rot.	Diff. for ring formation.
Formic acid + $(\text{CH}_2 \times 3) = 1.671 + 3.069 =$ .....	4.740	} - 0.599
Trimethylenecarboxylic acid .....	4.141	
Acetic acid + $(\text{CH}_2 \times 3) = 2.525 + 3.069 =$ .....	5.594	} - 0.546
Tetramethylenecarboxylic acid .....	5.048	
Propionic acid + $(\text{CH}_2 \times 3) = 3.462 + 3.069 =$ ...	6.531	} - 0.640
Pentamethylenecarboxylic acid .....	5.891	
Valeric acid + $(\text{CH}_2 \times 3) = 5.513 + 3.069 =$ .....	8.582	} - 0.607
Methylhexamethylenecarboxylic acid .....	7.975	

From these comparisons, it is seen that the numbers all approximate closely to  $-0.60$ .

If we compare the esters of the dibasic acids in the same manner, analogous, although somewhat lower, differences are obtained, the first comparison beginning, in this case, with diethyl oxalate, then with diethyl malonate, and so on :

	Mol. rot.	Diff. for ring formation.
Diethyl oxalate + $(\text{CH}_2 \times 3) = 6.654 + 3.069 =$ .....	9.723	} - 0.557
Diethyl trimethylenedicarboxylate* .....	9.166	
Diethyl malonate + $(\text{CH}_2 \times 3) = 7.410 + 3.069 =$ .....	10.479	} - 0.539
Diethyl tetramethylenedicarboxylate† .....	9.940	

Again, the ketones give similar results :

	Mol. rot.	Diff. for ring formation.
Acetone + $(\text{CH}_2 \times 3) = 3.516 + 3.069 =$ .....	6.585	} - 0.684
Tetramethylene methyl ketone‡ .....	5.901	
Methyl ethyl ketone + $(\text{CH}_2 \times 3) = 4.452 + 3.069 =$ .....	7.521	} - 0.610
Tetramethylene ethyl ketone§ .....	6.911	

Why tri- and tetra-methylene compounds should, throughout, behave in a manner analogous to the two first members in the aliphatic series, it is difficult at present to understand, but the results of the comparison are so constant and striking that there can hardly be a doubt as to the correctness of the view advanced.

Taking the average of the foregoing, we get for the ring formation with loss of  $\text{H}_2$ , a difference of  $0.6$  in acids, esters, and ketones.

In the case of hydrocarbons, this value is evidently much larger, as is seen from the comparison of hexane and hexamethylene :

Hexane .....	6.646	} - 0.982
Hexamethylene .....	5.664	

\* Trans., 1887, 51, 853.

† Trans., 1887, 51, 4.

‡ Trans., 1892, 61, 48.

§ Trans., 1892, 61, 52.

Although hexamethylene is the only substance of this class which has, so far, been examined, it will be shown in this paper that this large value of 0.982 is probably correct in other similar cases.

If, now, we compare hexamethylene with tetrahydrobenzene, we get

Tetrahydrobenzene .....	6.392	} + 0.734
Hexamethylene .....	5.658	

This +0.734 is the difference for unsaturation in these ring compounds, and is practically the same as that found in the case of open chain hydrocarbons (0.720).

On chlorinating hexamethylene, a remarkable result is obtained, the product losing its very low rotation and showing the difference for ring formation exhibited in the case of acids, esters, and ketones:

Propyl chloride.....	5.056
CH <sub>2</sub> × 3 .....	3.069
	<hr/>
	8.125
Chlorohexamethylene .....	7.489
	<hr/>
Value for ring formation.....	-0.636

The second displacement by chlorine changes the character of the rotation again, making the influence of the ring formation still smaller, thus:

Propylene dichloride, C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub> ...	6.344
CH <sub>2</sub> × 3 .....	3.069
	<hr/>
Calculated rotation of C <sub>6</sub> H <sub>12</sub> Cl <sub>2</sub> ...	9.413
Dichlorohexamethylene found ...	8.930
	<hr/>
Value for ring formation ...	-0.487

This value is practically the same as the value of H<sub>2</sub> in the aliphatic series (0.508) (see Trans., 1884, 45, 572); this is remarkable, as, besides the loss of H<sub>2</sub>, ring formation has also taken place.

From what has been said, it is seen that ring formation influences the rotation, as follows:

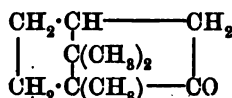
In hydrocarbons .....	-0.982
„ monochloro-substitution products, ketones, acids, and esters .....	-0.600
„ disubstitution products of ring hydrocarbons containing chlorine .....	-0.500

The difference of rotation shown by unsaturated substances and closed chain compounds is very remarkable, and has repeatedly proved

of the greatest value in deciding whether a new substance belonged to one class or to the other.

Since, then, the formation of saturated ring compounds from saturated substances containing two atoms of hydrogen more in the molecule is associated with the above-mentioned reduction in rotation, it became of interest to consider the case of the formation of so-called double or *bridged* rings, in which the ring formation from the open chain compound has taken place twice, and therefore with the loss of *four* atoms of hydrogen.

The most convenient of such bridged ring compounds for this purpose is ordinary camphor,  $C_{10}H_{16}O$ , since the results of extended investigation leave but little doubt that this substance has the constitution



originally assigned to it by Bredt (*Ber.*, 1893, 26, 3947).

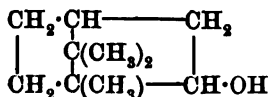
The magnetic rotation of camphor was therefore determined and found to be 9.265, and from this number and the following considerations we may obtain a fairly accurate value for the effect of bridged ring formation in this case.

The saturated open chain ketone in the aliphatic series corresponding with camphor would have the formula  $C_{16}H_{20}O$ , and its value may be calculated thus :

Methyl hexyl ketone .....	8.509
$\text{CH}_2 \times 2$ .....	2.046
Calc. rotation of ketone, $C_{10}H_{20}O$ .....	10.555
Found rotation of camphor, $C_{10}H_{16}O$ .....	9.265
Difference .....	-1.290

This difference, due of course to the formation of the double or *bridged* ring, is a *minus* one, and is, in fact, of a nature similar to that observed in the formation of a single ring (see above); it is therefore most interesting to note that by dividing the difference by 2, 0.645 is obtained, or a number closely agreeing with the average value for the influence of single ring formation in the case of ketones, &c., namely, -0.60 (see p. 294).

A similar result is obtained from an examination of the magnetic rotation of borneol. The constitution of this substance is represented by the formula



and, as it is related to camphor in the same way as a secondary alcohol is to a ketone, we should expect in the first place to find the rotations of these compounds differing by about 0.525\*.

The rotation of borneol calculated from that of camphor would then be camphor 9.265 + 0.525 = 9.790, a number closely agreeing with 9.807, which is the value actually observed.

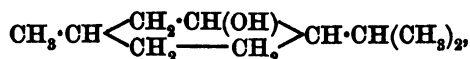
If now we proceed, as we did in the case of camphor, to calculate the effect of *bridged ring formation*, in passing from the corresponding saturated compound,  $C_{10}H_{22}O$ , to borneol we obtain the following figures.

The value of an open chain saturated secondary alcohol of the formula  $C_{10}H_{22}O$  may be calculated thus :

sec. Octyl alcohol .....	9.034
$CH_2 \times 2$ .....	2.046
	<hr/>
Value for $C_{10}H_{22}O$ calc. ....	11.080
Mag. rot. of borneol.....	9.807
	<hr/>
Difference ... ..	- 1.273

This value for the effect of bridged ring formation agrees closely with that deduced from camphor, namely, -1.290.

It is next of interest to study the case of menthol,



because, although it is very similar in constitution to camphor and borneol, it differs from them in being a single closed chain compound, the bridged ring being absent.

The rotation of menthol was found to be 10.486, and if we deduct this from the magnetic rotation of the corresponding saturated open chain alcohol,  $C_{10}H_{22}O$ , which, as shown above, is about 11.080, we obtain  $11.080 - 10.486 = 0.594$ , for the effect of a single ring formation, but as menthol contains the *isopropyl* group, the calculated number should, perhaps, be about 0.100 higher; this would make this difference 0.694. This number is only a little higher than the average value found in the synthetically prepared ring compounds, namely, 0.60 (see p. 294).

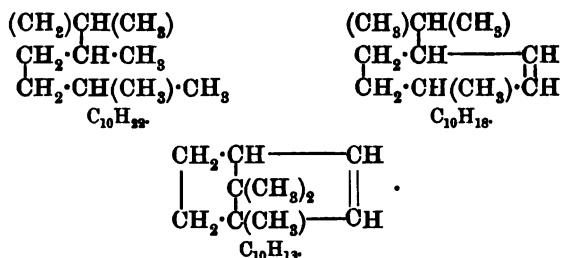
Turning next to the case of the terpenes,  $C_{10}H_{16}$ , the magnetic rotations of *l*-limonene, carvene (*d*-limonene), camphene, and pinene, have been determined and the results are given in the paper.

If we first consider the formula of camphene, the actual value of

\* This is the difference between the value of the rotation of *sec.* octyl alcohol,  $CH_3 \cdot [CH_2]_7 \cdot CH(OH) \cdot CH_3$ , 9.034, and that of methyl hexyl ketone,  $CH_3 \cdot [CH_2]_6 \cdot CO \cdot CH_3$ , 8.509.

bridged ring formation in a hydrocarbon of this class may be deduced in the following way.

It may be assumed that camphene is produced from an open chain compound,  $C_{10}H_{22}$ , by first converting it into a six carbon unsaturated ring,  $C_{10}H_{18}$ , and then subsequently forming the bridged ring, as indicated by the following formulæ :



The calculation of the value for the formula  $C_{10}H_{22}$  is a simple one, and may be carried out as follows :

Heptane.....	7.669
$CH_2 \times 3$ .....	3.069

Calculated value of  $C_{10}H_{22}$  ..... 10.738

The use of this calculation in the present case requires some explanation. It has been shown (p. 297) that when  $CH_2$  is introduced into an aliphatic hydrocarbon to form the next homologue, the normal chain has a rotation which is lower, by about  $-0.1$ , than that of the isomeric compound containing a side chain. Thus, starting with *n*-pentane,  $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$  (mag. rot. 5.638), *n*-hexane,  $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ , has a rotation of 6.670, whereas the rotation of *isohexane*,  $(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot CH_3$ , is 6.769, a difference of 0.099. This behaviour is shown in all similar cases in the aliphatic series.

On the other hand, in ring compounds the introduction of  $CH_2$ , whether it enters the ring or forms a side chain consisting of a methyl group, produces the same, or nearly the same, effect on the rotation, thus :

(a) Pentamethylenecarboxylic acid ..	$CH_2 \begin{array}{l} \diagup CH_2 \cdot CH_2 \\ \diagdown CH_2 \cdot CH \cdot CO_2H \end{array}$	5.891
(b) Methylpentamethylenecarboxylic acid .....	$CH_2 \begin{array}{l} \diagup CH_2 \cdot CH \cdot CH_2 \\ \diagdown CH_2 \cdot CH \cdot CO_2H \end{array}$	6.914
(c) Methylhexamethylenecarboxylic acid .....	$\begin{array}{l} CH_2 \cdot CH_2 \cdot CH \cdot CH_2 \\ CH_2 \cdot CH_2 \cdot CH \cdot CO_2H \end{array}$	7.973

In the case of the formation of *b*, it may be assumed that the  $\text{CH}_3$  has entered into *a* to form a *side chain* consisting of a methyl group, and the result is an increase in the mag. rot. of 1.023. In the formation of *c* from *b*,  $\text{CH}_2$  enters into the *ring*; the increase in magnetic rotation is 1.061, or about the same value in both cases. In calculating the value for a ring formula such as that of camphene, it may therefore be taken that the differences for  $\text{CH}_2$  are about 1.023, whether the  $\text{CH}_2$  enters the ring or gives rise to the formation of a methyl group.

The actual value of the formula  $\text{C}_{10}\text{H}_{22}$  given above would evidently be higher than 10.738 on account of the methyl side chains which it contains, but as all of these ultimately enter into the ring of camphene, this extra influence peculiar to methyl groups in the open chain compounds must be neglected.

Referring again to the calculation of the magnetic rotation of camphene from that of the hydrocarbon  $\text{C}_{10}\text{H}_{22}$ , the first process indicated by the two formulæ,



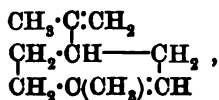
can be easily followed, since the analogous relationships between hexene and tetrahydrobenzene,



have been investigated.

The magnetic rotation of hexane is 6.646, and that of tetrahydrobenzene is 6.392; it follows, therefore, that the value for the formation of the unsaturated six carbon ring is -0.254. Applying this to the case of camphene, it was shown on page 298 that the calculated value of the saturated hydrocarbon,  $\text{C}_{10}\text{H}_{22}$ , is 10.738; if, therefore, we deduct -0.254 from this, we obtain 10.484 as the value of the unsaturated six carbon ring,  $\text{C}_{10}\text{H}_{18}$ . Since, then, the observed magnetic rotation of camphene is 10.135, it follows that the influence of bridging the ring in this hydrocarbon is represented by the value  $10.484 - 10.135 = 0.349$ . The value of the bridged formation in this compound must then be  $-0.982 + 0.349 = -1.331$ , which is not very different from that found in the case of camphor, -1.290.

Having obtained this value, 0.349, for bridging the ring, it is possible to estimate the probable rotation of terpenes such as *limonene*,



and it will be at once seen that both limonene and camphene contain their carbon atoms in the same order, and may be said to be derived from almost identical saturated hydrocarbons of the formula  $C_{10}H_{22}$ . Both camphene and limonene contain a six carbon unsaturated ring, and the essential difference between the two is that in the former the group  $CH_2 \cdot CH \cdot CH_2$  has lost two atoms of hydrogen on entering into this ring in a form of a bridge, whereas in the latter this loss of two atoms of hydrogen has resulted in the conversion of the group into the unsaturated group  $CH_2 \cdot CH : CH_2$ , which remains outside the ring.

In order to deduce the value of limonene from that of camphene, we must deduct the value for bridging the ring ( $-0.349$ ), and add the value for the conversion of the saturated group into the corresponding unsaturated one ( $+0.720$ , see p. 295), thus :

Rotation of camphene .....	10.136
Deduct value of ring formation, ( $-0.349$ ), i.e., add	$+0.349$
Add for unsaturation .....	$+0.720$
<hr/>	
Calculated mag. rotation of limonene.....	11.205

It is certainly interesting that the number thus calculated coincides nearly exactly with that actually found, as the average value of *l*-limonene and *d*-limonene (carvene) is 11.204.

The rotation of the limonenes may be calculated in another manner, and with almost identical results, thus :

Calculated value of the hydrocarbon $C_{10}H_{22}$ .....	10.738
Less single ring formation of hydrocarbon (see p. 295)...	0.982
<hr/>	
	9.756
Amount for unsaturation outside ring .....	$+0.720$
"                      "          inside ring .....	$+0.720$
<hr/>	
	11.196

This is again almost identical with the number, 11.204, actually obtained.

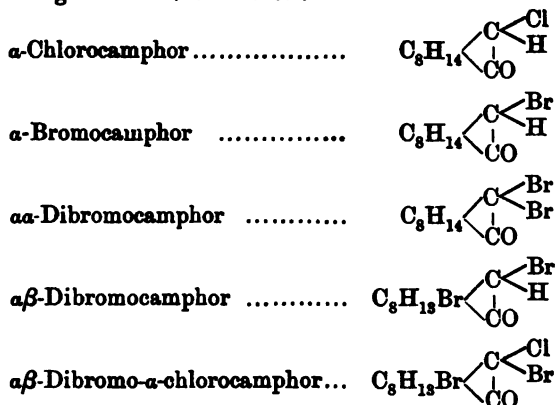
These considerations make it probable that the determination of the magnetic rotation of a terpene of unknown constitution may prove of considerable value in deciding its formula, as this will show clearly whether it belongs to the camphene class (compare Marsh, Proc., 1899, 54, and Semmler, Ber., 1900, 33, 3420) and contains a bridged, unsaturated ring, or whether, like limonene, it is doubly unsaturated and the bridged ring is absent; in the former case, the value would approximate to 10.133, in the latter to 11.204.

*Pinene*, although isomeric with camphene, is not so closely related to

camphor, since the camphor bridged ring is still intact in camphene whereas in the case of pinene, the bridged ring is of a somewhat different kind. The general similarity between camphene and pinene is, however, indicated by the comparatively slight difference in the magnetic rotation, namely, +0.159.

*Chloro- and Bromo-substitution Derivatives of Camphor.*

The following have been examined :



The first influence of chlorine and bromine when it displaces hydrogen in camphor is as follows :

$\alpha$ -Chlorocamphor ...	10.846	$\alpha$ -Bromocamphor ...	12.761
Camphor .....	9.265	Camphor .....	9.265
Cl displacing H ...	1.581	Br displacing H ...	3.496

The values for the halogens displacing hydrogen in open chain compounds fluctuate a good deal (see Trans., 1894, 65, 417, 418), but the above numbers are abnormally high. The highest observed values in open chain compounds for monochloro- and monobromo-derivatives are 1.470 and 3.424 respectively. When a further displacement of hydrogen by bromine occurs in camphor, the values are nearly normal for the second substitution, as the following comparisons will show :

$\alpha\alpha$ -Dibromocamphor	15.994	$\alpha\beta$ -Dibromocamphor	15.902
$\alpha$ -Bromocamphor ...	12.761	$\alpha$ -Bromocamphor ...	12.761
Br displacing H ...	3.233	Br displacing H ...	3.141

As will be seen, the  $\alpha\beta$ -compound gives the smaller number of the two.



Lastly, coming to a third displacement, the result is again about normal:

$\alpha\beta$ -Dibromo- $\alpha$ -chlorocamphor .....	17.346
$\alpha\beta$ -Dibromocamphor .....	15.902
Cl displacing H.....	1.444

The high values found for the monochloro- and monobromo-compounds were what might be expected, as it has been shown that the same thing occurs in hexamethylene, only to a greater extent, the value for the chlorine atom, which displaces hydrogen in the latter case, being no less than 1.843. The second displacement by the halogen is, however, about normal, just as when the second atom of hydrogen in camphor is displaced by bromine.

*$\alpha$ -Nitrocamphor, pseudo-Nitrocamphor, Camphoryloxime, and Anhydro-pseudonitrocamphor.*

It will be convenient to consider the rotation of these substances together.

Nitrocamphor, compared with camphor, shows the following difference in rotation:

$\alpha$ -Nitrocamphor.....	9.468
Camphor .....	9.265
$\text{NO}_2$ disp. H .....	0.203

This difference is similar to, although a little lower than, that noticed between nitropropane and propane, which is 0.229 (Trans., 1889, 55,729).

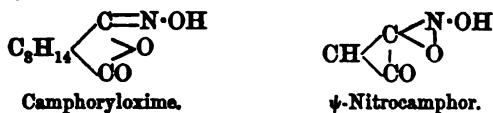
After obtaining this result, experiments were made with the view of comparing the rotations of nitrocamphor and *pseudonitrocamphor*. Dr. Lowry considers that these two substances are represented by the formulæ:



As the latter cannot be isolated in a pure condition, it was necessary to examine one of its stable salts, and, after trials with several of these, the triethylamine compound was selected as most suitable. The rotation of the *pseudonitro*-compound, after allowing for the triethylamine, was found to be 10.469 (see p. 313), a number which is considerably higher than that of nitrocamphor, thus:

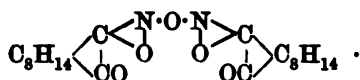
$\psi$ -Nitrocamphor .....	10.469
$\alpha$ -Nitrocamphor .....	9.468
	1.001

As it has been found that the magnetic rotations of amides and oximes are identical (unpublished results), it was of interest to compare those of the *pseudonitro*-compound and camphoryloxime, which are related as follows :



and it was found that their values were very similar, that of the oxime being 10.375.

As the relationship between the rotation of the acids and anhydrides is known, it is possible to get a second value for the rotation of the *pseudonitro*-compound by determining that of the anhydride which is stable, and has the formula :



Its rotation was found to be 19.712.

The difference between the rotation of the anhydride of a monobasic acid and that of 2 mols. of the acid it is derived from is 9.752 ; if this then be added to the rotation of the anhydride, the result will be the rotation of 2 mols. of *pseudonitro*camphor, and if this be divided by 2 it will give the rotation of this compound itself :

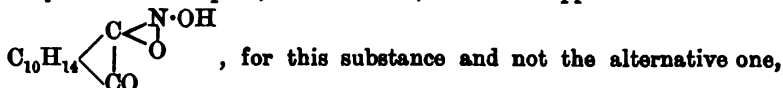
Anhydride of $\psi$ -nitrocamphor .....	19.712
Difference between anhydride and 2 mols. of acid ...	0.752
Rotation of 2 mols. $\psi$ -nitrocamphor .....	<u>2/20.464</u>
$\psi$ -Nitrocamphor .....	10.232

This is only a little lower than that obtained from the triethylamine salt. Considering the probable experimental errors connected with this kind of comparison, the average of all will probably not be far from the truth ; it amounts to 10.346, a value which is nearly identical with that of its isomeride, camphoryloxime.

It would appear, therefore, that the difference between the rotation of the normal and the *pseudonitro*-compounds amounts to about 1.00, because the numbers for the nitro-compound are undoubtedly a little high on account of the solution examined containing a small quantity of the pseudo-form, as pointed out by Lowry. It is also interesting to find that the rotations of the pseudo-compound and the isomeric oxime are identical, and it affords another instance of the use of the magnetic rotations in distinguishing between two forms of nitro-compounds such as these.

The change of optical rotation which takes place when nitrocamphor is converted into the pseudo-form is very remarkable. In ethylene chloride solution, nitrocamphor has a rotation of  $[\alpha]_D -19.47^\circ$ , whereas the rotation of  $\alpha$ -nitrocamphor, calculated from the aqueous solution of the triethylamine salt, is no less than  $[\alpha]_D +345.5^\circ$ . Cazeneuve found for the sodium salt  $[\alpha]_D +298^\circ$  (*Bull. Soc. Chim.*, 1888, [ii], 49, 92).

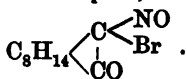
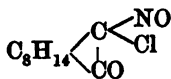
There is one interesting point connected with the magnetic rotation of *pseudonitrocamphor*, and that is, that it supports the formula



$\text{C}_{10}\text{H}_{14} \begin{array}{c} \diagup \text{C} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C} \cdot \text{NO} \cdot \text{OH}$ . One essential difference between these formulæ is that the first represents the nitrogen as tervalent, and the second as quinquivalent, and it has been shown that these two conditions of nitrogen influence the magnetic rotation of substances containing nitrogen very differently, the former by about 0.611 and the latter by only 0.103, the variation being practically 0.500 (*Trans.*, 1889, 55, 737).

Now the rotation of *pseudonitrocamphor*, as seen above, being identical or nearly so with that of its isomeride camphoryloxime, which contains tervalent nitrogen, the inference therefore is that this *pseudonitro*-compound must also contain it in that condition; if it were quinquivalent, the rotation should be about 0.50 lower than that of camphoryloxime, which is a very large difference.

*aa'-Chloro- and aa'-Bromo-nitrocamphor,*



It has already been pointed out that in nitrocamphor the influence of the substitution of the nitro-group for hydrogen is +0.203, being slightly less than the value found in the case of the conversion of propane into nitropropane (0.229). In chloronitrocamphor, the  $\text{NO}_2$  group is slightly negative, and in bromonitrocamphor, negative to a still greater extent. It has, in fact, been found that as the specific rotation of substances increases, the influence of this group, which is always small, diminishes; the positive nature of the value in substances of small specific rotation becoming negative in substances of large specific rotation, thus, for example, in the case of chloroform, which has a rather large specific rotation, nitropicrin, derived from it by the

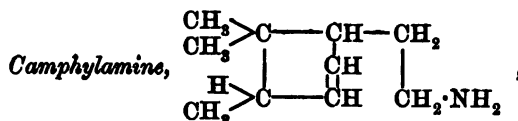
substitution of  $\text{NO}_2$  for hydrogen, has a smaller rotation than chloroform itself, thus :

Chloroform .....	5.559
Nitropicrin .....	5.384
Difference .....	-0.175

and this has been observed in several other instances, the particulars of which have not yet been published. Chloronitrocampa<sup>h</sup>or having a larger specific rotation than camphor, the introduction of the  $\text{NO}_2$  group yields a nitro-compound in which the influence of this group is slightly negative, and again, bromonitrocampa<sup>h</sup>or has a larger specific rotation than chlorocampa<sup>h</sup>or, and as a result, the nitro-compound gives a value still more negative. The following table shows the rotation of these nitro-compounds compared with that of the substances from which they are derived :

Camphor .....	9.265	} +0.203
$\alpha$ -Nitrocampa <sup>h</sup> or .....	9.468	
$\alpha$ -Chlorocampa <sup>h</sup> or.....	10.846	} -0.024
$\alpha\alpha'$ -Chloronitrocampa <sup>h</sup> or ...	10.822	
$\alpha$ -Bromocampa <sup>h</sup> or.....	12.761	} -0.041
$\alpha\alpha'$ -Bromonitrocampa <sup>h</sup> or ...	12.720	

These results appear to be similar in character to those obtained with mixtures of substances with greatly varying specific rotations, to which I have previously drawn attention (Trans., 1896, 69, 1052).



(Tiemann, *Ber.*, 1897, 30, 245).

The magnetic rotation of this base was found to be 11.770, and it is evidently an unsaturated ring compound. The rotation of the saturated aliphatic base corresponding with camphylamine is  $\text{C}_{10}\text{H}_{23}\text{N}$ ; its rotation may be calculated thus :

Propylamine, $\text{C}_3\text{H}_9\text{N}$ .....	4.563
$\text{CH}_2 \times 7 = 1.023 \times 7 =$ .....	7.161
Rotation of $\text{C}_{10}\text{H}_{23}\text{N}$ .....	11.724

The influence of unsaturation may be calculated from the difference of rotation betweenallylamine and propylamine, namely, 5.587 - 4.563 = 1.024. If this be added to the above, the rotation of this base, sub-

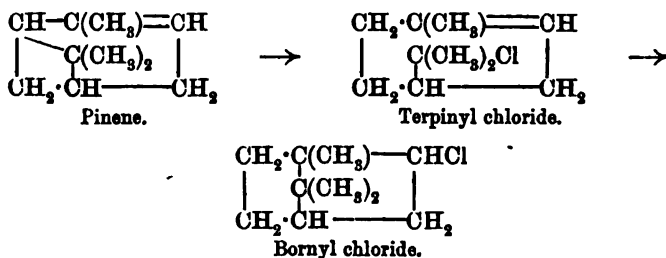
tracted from the rotation of camphylamine, will leave a value representing the influence of the ring formation, thus :

$C_{10}H_{23}N$ .....	11.724
For unsaturation .....	1.024
	<hr/>
	12.748
Rotation of camphylamine .....	11.770
	<hr/>
Ring formation.....	0.978

It is interesting to find that this number for ring formation is practically the same as that observed in the case of hydrocarbons (0.982).

*Bornyl Chloride (Pinene Hydrochloride),  $C_{10}H_{17}Cl$ .*

The magnetic rotation of this compound was found to be 11.058, and if from this we deduct the rotation of pinene, 10.294, we obtain a difference = 0.764. This difference, however, does not represent that of hydrogen chloride merely, because pinene, when converted into its hydrochloride, becomes a saturated compound; it is therefore necessary to add to this number (0.764) the amount which is lost by this change, namely, 0.720, the value for unsaturation (see p. 295); this gives 1.484. Since the value of HCl is 1.987, the discrepancy of - 0.503 points to the fact that pinene undergoes some further change in structure when it is converted into the hydrochloride, and not merely that resulting from its becoming a saturated compound in union with hydrogen chloride. Wagner and Brickner (*Ber.*, 1900, 32, 2325) have recently shown that pinene hydrochloride is not, as formerly supposed, a derivative of pinene, but is bornyl chloride, molecular change having taken place during the addition of hydrogen chloride, thus:



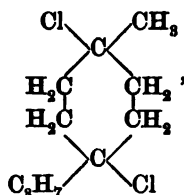
That this view is in accordance with the results of the magnetic rotation determinations may be shown as follows.

The rotation of *sec*.octyl alcohol is 9.004 and that of *sec*.octyl chloride is 10.248, showing that, in passing from a secondary

alcohol to the corresponding chloride, there is a rise of rotation of 1.224. If, then, pinene hydrochloride is bornyl chloride, its rotation should easily be calculated by adding to the rotation of the corresponding secondary alcohol, borneol (9.806), the number 1.244. This gives 11.050 as the calculated rotation of bornyl chloride, which agrees almost exactly with that found, namely, 11.058.

*trans-Dipentene Dihydrochloride*,  $C_{10}H_{16}, 2HCl$ .

The magnetic rotation of this compound, which, according to Baeyer (*Ber.*, 1893, 26, 2862), has the formula :



has been found to be 13.111. This formula represents the substance  $C_{10}H_{16}Cl_2$  as a dichloromethylisopropylhexamethylene, and its rotation may be calculated thus :

Dichlorohexamethylene .....	8.906
$CH_2 \times 4 = 1.023 \times 4 =$ .....	4.092
Addition for <i>iso</i> -group .....	0.103
Calculated rotation of $C_{10}H_{16}Cl_2$ .....	13.101

It will be seen that the number found agrees closely with that calculated in this way.

*Refraction values of Camphor and its Compounds.*

The results of these determinations, the particulars of which will be found in the experimental part of this paper, are in most cases lower than the calculated, as will be seen from the following table, which gives the differences between the theoretical and observed values for  $\frac{\mu_a - 1}{d} \rho$ .

Borneol .....	- 0.409	$\alpha\beta$ -Dibromo- $\alpha$ -chloro-	
Camphor .....	+ 0.154	camphor .....	- 0.560
$\alpha$ -Chlorocamphor .....	- 0.150	$\alpha$ -Nitrocarnphor.....	- 0.045
$\alpha$ -Bromocamphor .....	- 0.207	$\alpha\alpha'$ -Chloronitrocarnphor	- 0.522
$\alpha\alpha$ -Dibromocamphor....	- 0.436	$\alpha\alpha'$ -Bromonitrocarnphor	- 0.768
$\alpha\beta$ -Dibromocamphor ...	- 0.808	Camphoryloxime .....	+ 0.812

The comparison of these results with the magnetic rotation determinations is a matter of difficulty, but so far as it has been carried out the variation in the two values seem to be of the same nature except in the case of camphor.

There is a certain analogy between the refractive values of  $\alpha$ -nitro-camphor,  $\alpha\alpha'$ -chloronitrocamphor, and  $\alpha\alpha'$ -bromonitrocamphor, inasmuch as that, whilst the nitro-compound has a refractive value nearly the same as the calculated, the chloro-derivative has a considerably lower, and the bromo-derivative a still lower value, these differences being in the same order as the magnetic rotation. In the case of camphoryloxime, it is also found that its refractive value is higher than that of its isomeride,  $\alpha$ -nitrocamphor, a result similar to that found in the case of their magnetic rotations.

#### EXPERIMENTAL.

It will be seen from this part of the paper that as all the camphor compounds are solids and not easily fusible, they had to be examined in solution. A very good solvent for those examined is chloroform, but owing to its volatility it is difficult to keep the solutions of constant composition for any length of time. Ethylene chloride was therefore tried and found to be an excellent solvent; and as its boiling point is  $83.5^\circ$ , it was much more suitable than chloroform; moreover, its specific rotation was found not to vary very largely from those of the camphor compounds, experiment showing that it is a little higher than those of camphor, its nitro- and chloro-derivatives, and a little lower than those of the bromo-derivatives. The error, therefore, arising from this cause would be small, it having been found that in the magnetic rotation of mixtures a reduction occurs more or less proportional to the difference between the specific rotations of the constituents.

A litre of ethylene chloride, purified by shaking with concentrated sulphuric acid several times, was washed, and after being dried first with potassium carbonate, and then with phosphoric oxide, was filtered and distilled. It all came over within less than half a degree, and when fractionated into three quantities, the densities of the first and third only differed by 0.00018. The density at  $15^\circ$  was 1.26197, this is higher than that previously observed, both by Thorpe and myself, by about 0.0021 (Trans., 1884, 45, 528), and is probably due to the greater purity obtained by treatment with sulphuric acid.

The magnetic rotation was determined on three occasions and gave :

t.	Sp. rot.	Mol. rot.
$18.7^\circ$	1.2564	5.496

With specimens previously examined, the mol. rotation obtained was 5.485, which is practically the same as that now found.

Solutions made with this solvent were preserved in bottles with stoppers moistened with glycerine, and were found to undergo practically no change, even after being kept for months, as was proved by redetermining their densities.

The solutions were made as concentrated as possible, but on account of the varying solubilities of the camphor compounds, they could not be made of similar strengths.

*Menthol*,  $C_{10}H_{20}O$ .

This substance was examined in the fused state.

Density :  $d$  40°/40°, 0.8909 ;  $d$  45°/45°, 0.8888 ;  $d$  50°/50°, 0.8868 ;  $d$  55°/55°, 0.8850 ;  $d$  60°/60°, 0.8835 ;  $d$  65°/65°, 0.8820.

Magnetic rotation determined on three different occasions :

	t.	Sp. rot.	Mol. rot.
Average.....	45.2°	1.0754	10.486

Optical rotation at 47°  $[\alpha]_D = -49.88^\circ$

*Borneol*,  $C_{10}H_{18}O$ .

This was redistilled before use, b. p. 214° under 772 mm. pressure.

The strongest solution that could be used contained 23.728 per cent., the composition being  $C_{10}H_{18}O + 5$  mols.  $C_2H_4Cl_2$ .

Density :  $d$  10°/10°, 1.1819 ;  $d$  15°/15°, 1.1750.

Magnetic rotation determined on three different occasions :

	t.	Sp. rot.	Mol. rot.
Average.....	15.8°	1.2122	37.232
Less 5 mols. $C_2H_4Cl_2$ .....			27.425
Mol. rot. $C_{10}H_{18}O$ .....			9.807

Optical rotation  $[\alpha]_D = +35.22^\circ$

*Camphor*,  $C_{10}H_{16}O$ .

This substance was redistilled for examination. Two solutions in ethylene chloride were used.

The first contained 50.582 per cent., representing in composition,  $C_{10}H_{16}O + 1.50$  mols.  $C_2H_4Cl_2$ .

Density :  $d$  10°/10°, 1.0985 ;  $d$  15°/15°, 1.0939.



Magnetic rotation twice determined :

	t.	Sp. rot.	Mol. rot.
Average.....	11.72°	1.1483	17.478
Less 1.5 mols. $C_2H_4Cl_2$ .....			8.227
			<hr/>
$C_{10}H_{16}O$ .....			9.251

Optical rotation  $[\alpha]_D = +51.936^\circ$ .

The second contained 67.18 per cent., representing  $C_{10}H_{16}O + 0.75$  mol.  $C_2H_4Cl_2$ . This was a practically saturated solution at the ordinary temperature.

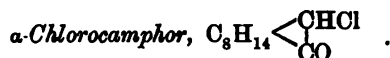
Density :  $d_{10^\circ/10^\circ}$ , 1.0523 ;  $d_{15^\circ/15^\circ}$ , 1.0489.

Magnetic rotation ; four times determined :

	t.	sp. rot.	Mol. rot.
Average.....	15.74°	1.1171	13.393
Less 0.75 mol. $C_2H_4Cl_2$ .....			4.113
			<hr/>
$C_{10}H_{16}O$ .....			9.280

Optical rotation  $[\alpha]_D = +52.68^\circ$ .

The magnetic rotations of both solutions being very close, the average, 9.265, has been taken as correct.



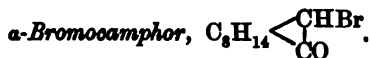
The solution employed contained 32.017 per cent. of *α*-chlorocamphor, the composition being  $C_{10}H_{15}OCl + 4$  mols.  $C_2H_4Cl_2$ .

Density :  $d_{10^\circ/10^\circ}$ , 1.2154 ;  $d_{15^\circ/15^\circ}$ , 1.2102.

Magnetic rotation determined on three separate occasions :

	t.	Sp. rot.	Mol. rot.
Average.....	12.4°	1.2288	32.786
Less 4 mols. $C_2H_4Cl_2$ .....			21.940
			<hr/>
Mol. rot. $C_{10}H_{15}OCl$ .....			= 10.846

Optical rotation  $[\alpha]_D = +106.5^\circ$ . Lowry found (in alcohol)  $+96^\circ$ .



The solution used contained 43.75 per cent. of this substance, the composition being  $C_{10}H_{15}OBr + 3$  mols.  $C_2H_4Cl_2$ .

Density :  $d_{10^\circ/10^\circ}$ , 1.3047 ;  $d_{15^\circ/15^\circ}$ , 1.2993.

Magnetic rotation determined on three occasions :

	t.	Sp. rot.	Mol. rot.
Average.....	12.2°	1.2972	29.216
Less 3 mols. C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> .....			16.455
			<hr/>
Mol. rot. C <sub>10</sub> H <sub>15</sub> OBr .....			12.761

Optical rotation  $[\alpha]_D = +145.34^\circ$ . Lowry found (in alcohol)  $+135^\circ$ .



The solution of this compound was not so concentrated as that of the mono-derivative ; it contained 34.292 per cent., the composition being C<sub>10</sub>H<sub>14</sub>OBr<sub>2</sub> + 6 mols. C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>.

Density :  $d_{10^\circ/10^\circ}$ , 1.3825 ;  $d_{15^\circ/15^\circ}$ , 1.3764.

Magnetic rotation determined on four separate occasions :

	t.	Sp. rot.	Mol. rot.
Average.....	15.52°	1.3397	48.904
Less 6 mols. C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> .....			32.910
			<hr/>
Mol. rot. C <sub>10</sub> H <sub>14</sub> OBr <sub>2</sub> .....			= 15.994

Optical rotation  $[\alpha]_D = +42.067^\circ$ . Lowry found (in chloroform)  $+40^\circ$ .



This substance did not dissolve very freely ; the solution used contained 25.812 per cent. Composition C<sub>10</sub>H<sub>14</sub>OBr<sub>2</sub> + 9 mols. C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>.

Density :  $d_{10^\circ/10^\circ}$ , 1.3388 ;  $d_{15^\circ/15^\circ}$ , 1.3528.

Magnetic rotation determined on five occasions :

	t.	Sp. rot.	Mol. rot.
Average.....	14.9°	1.3234	65.266
Less 9 mols. C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> .....			49.364
			<hr/>
Mol. rot. C <sub>10</sub> H <sub>14</sub> OBr <sub>2</sub> .....			= 15.902

Optical rotation  $[\alpha]_D = +104.167^\circ$ .



The solution of this substance employed contained 36.668 per cent., the composition being C<sub>10</sub>H<sub>13</sub>OCBr<sub>2</sub> + 6 mols. C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>.

Density :  $d_{10^\circ/10^\circ}$ , 1.4181 ;  $d_{15^\circ/15^\circ}$ , 1.4122.

Magnetic rotation determined on two occasions :

	t.	Sp. rot.	Mol. rot.
Average.....	13.1°	1.3633	50.213
Mol. rot. 6 mols. $C_2H_4Cl_2$ .....			32.910
Mol. rot. $C_{10}H_{18}OClBr_2$ .....			-17.303

Optical rotation  $[\alpha]_D = +43.016^\circ$ . Lowry found (in chloroform)  $+44.5^\circ$ .

*Camphylamine*,  $C_{10}H_{19}N$ .

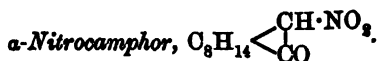
This substance boiled at  $205.5-206.5^\circ$  corr. (b. p. given in Beilstein, 194—196°).

Density :  $d_{15^\circ/15^\circ}$ , 0.8729 ;  $d_{20^\circ/20^\circ}$ , 0.8697 ;  $d_{25^\circ/25^\circ}$ , 0.8669.

Magnetic rotation determined on three different occasions :

	t.	Sp. rot.	Mol. rot.
Average .....	16°	1.2078	11.770

This substance had a small + optical rotation.



For this and the other camphor derivatives, I am indebted to Dr. Lowry. This substance was examined in two solutions. In the second solution, it was examined as soon as possible after being made.

The first solution contained 49.873 per cent. of nitrocamphor. Composition,  $C_{10}H_{18}O\cdot NO_2 + 2$  mols.  $C_2H_4Cl_2$ . It was several days old when examined.

Density :  $d_{10^\circ/10^\circ}$ , 1.20982 ;  $d_{15^\circ/15^\circ}$ , 1.20491.

Magnetic rotation determined on three different occasions :

	t.	Sp. rot.	Mol. rot.
Average.....	12.14°	1.1246	20.438
Less 2 mols. $C_2H_4Cl_2$ .....			10.970
Mol. rot. $C_{10}H_{18}O\cdot NO_2$ .....			9.468

Optical rotation  $[\alpha]_D = 19.47^\circ$ .

The second solution contained 44.319 per cent. of nitrocamphor. Composition,  $C_{10}H_{18}O\cdot NO_2 + 2.5$  mols.  $C_2H_4Cl_2$ .

Density :  $d_{10^\circ/10^\circ}$ , 1.2166 ;  $d_{15^\circ/15^\circ}$ , 1.2117.

Magnetic rotation once determined with fresh solution :

t.	Sp. rot.	Mol. rot.
15.4°	1.1335	23.109
Less 2.5 mols. $C_2H_4Cl_2$ .....		13.712
		<hr/>
Mol. rot. $C_{10}H_{15}O \cdot NO_2$ ...		9.397

*$\alpha$ -Nitrocamphor, Triethylamine, and Water.*

The compound of triethylamine and nitrocamphor was used with the view of getting the rotation of *pseudonitrocamphor*. An excess of triethylamine was employed to ensure all the nitrocamphor being in combination. Experiments with piperidine as the base were also made, but the product crystallised out too readily when the solutions were strong.

The solution contained 36.532 per cent. of nitrocamphor. Composition,  $C_{10}H_{15}O \cdot NO_2 + 1.25$  mols.  $(C_2H_5)_3N + 12$  mols.  $H_2O$ .

Density :  $d$  15°/15°, 1.0468 ;  $d$  20°/20°, 1.0444.

Magnetic rotation, determined on three occasions a month apart :

	t.	Sp. rot.	Mol. rot.
Average.....	15.5°	1.1569	33.116
Less 12 mols. $H_2O$ .....			12.000
			<hr/>
			21.116
Less 1.25 mols. $(C_2H_5)_3N$ .....			10.647
			<hr/>
$C_{10}H_{15}O \cdot NO_2$ .....			10.469

The optical rotation of this solution, calculated on the nitrocamphor, was no less than  $[\alpha]_D + 345.5^\circ$ . Cazeneuve gives for the sodium salt  $[\alpha]_D + 298^\circ$ ; this of course would be higher if calculated on the nitrocamphor only, although not quite so high as the above ( $+331.2^\circ$ ).

*Anhydro- $\psi$ -nitrocamphor,  $C_{20}H_{28}O_5N_3$ .*

This substance is not very soluble in ethylene chloride, the strongest solution that could be conveniently used containing only 15.959 per cent. and having the composition  $C_{20}H_{28}O_5N_3 + 20$  mols.  $C_2H_4Cl_2$ .

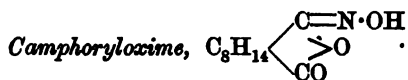
Density :  $d$  10°/10°, 1.2547 ;  $d$  15°/15°, 1.2488.

Magnetic rotation, four times determined on different occasions :

	t.	Sp. rot.	Mol. rot.
Average.....	14.9°	1.2348	129.412
Less 20 mols. $C_2H_4Cl_2$ .....			109.700
			<hr/>
Mol. rot. $C_{20}H_{28}O_5N_3$ .....			-19.712

### 31 PERKIN : MAGNETIC ROTATION OF RING COMPOUNDS.

Optical rotation  $[\alpha]_D = +132.84^\circ$ . Lowry gives for solution in benzene  $+187^\circ$ , and in chloroform  $+167^\circ$ .



A solution of this substance in ethylene chloride containing 44.319 per cent. was used. Composition,  $C_{10}H_{16}O_3N + 2.5$  mols.  $C_2H_4Cl_2$ .

Density:  $d_{15^\circ/15^\circ}$ , 1.2418;  $d_{20^\circ/20^\circ}$ , 1.2365.

Magnetic rotation, determined on three separate occasions:

	t.	Sp. rot.	Mol. rot.
Average.....	17.4°	1.2088	24.087
Less 2.5 mols. $C_2H_4Cl_2$ .....			13.712
			<hr/> 10.375

Optical rotation  $[\alpha]_D = 14.09^\circ$ . Lowry obtained, in a 5 per cent. solution in benzene,  $[\alpha]_D = 7.0^\circ$ .



The solution examined contained 43.803 per cent. of this substance. Composition,  $C_{10}H_{14}OCl \cdot NO_2 + 3$  mols.  $C_2H_4Cl_2$ .

Density:  $d_{10^\circ/10^\circ}$ , 1.2641;  $d_{15^\circ/15^\circ}$ , 1.2589.

Magnetic rotation, determined on two occasions:

	t.	Sp. rot.	Mol. rot.
Average.....	12.85°	1.1717	27.277
Less 3 mols. $C_2H_4Cl_2$ .....			16.455
			<hr/> 10.822
Mol. rot. $C_{10}H_{14}OCl \cdot NO_2$ ...			10.822

Optical rotation  $[\alpha]_D = 6.924^\circ$ . Lowry found (in chloroform)  $5^\circ$ .



The solution employed contained 31.724 per cent., the composition being  $C_{10}H_{14}OBr \cdot NO_2 + 6$  mols.  $C_2H_4Cl_2$ .

Density:  $d_{10^\circ/10^\circ}$ , 1.3288;  $d_{15^\circ/15^\circ}$ , 1.3231.

Magnetic rotation, determined on two occasions:

	t.	Sp. rot.	Mol. rot.
Average.....	12.7°	1.2516	45.630
Less 6 mols. $C_2H_4Cl_2$ .....			32.910
			<hr/>
Mol. rot. $C_{10}H_{14}OBr \cdot NO_2$ .....			12.720

Optical rotation  $[\alpha]_D =$

*l-Limonene*,  $C_{10}H_{16}$ .

For this hydrocarbon, as well as for the terpene derivatives referred to in this paper, I am indebted to Professor Tilden. It was purified in the same manner as mentioned below in reference to carvene. Its boiling point was 175.5—177° (corr.).

Density:  $d$  10°/10°, 0.8549;  $d$  15°/15°, 0.8514;  $d$  20°/20°, 0.8483;  $d$  25°/25°, 0.8453.

Magnetic rotation, determined on six different occasions:

t.	Sp. rot.	Mol. rot.
15°	1.2578	11.162

Optical rotation  $[\alpha]_D = -103.51^\circ$ .

*Carvene* or *d-Limonene*,  $C_{10}H_{16}$ .

Obtained from Kahlbaum. It was purified by steam distillation with alkali, then dried, and fractionated. The boiling point was 178—179° (corr.).

Density:  $d$  4°/4°, 0.8576;  $d$  10°/10°, 0.8532;  $d$  15°/15°, 0.8498;  $d$  25°/25°, 0.8437.

Magnetic rotation, determined on four occasions:

t.	Sp. rot.	Mol. rot.
16.32°	1.2637	11.246

Optical rotation  $[\alpha]_D = +122.7^\circ$ .

Average mol. rot. of *l*-limonene and carvene, 11.204.

*Pinene*,  $C_{10}H_{16}$ .

The specimen used had a boiling point of 158.5—159°.

Density:  $d$  4°/4°, 0.8740;  $d$  5°/5°, 0.8732;  $d$  10°/10°, 0.8694;  $d$  15°/15°, 0.8658;  $d$  20°/20°, 0.8624;  $d$  25°/25°, 0.8595.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
20°	1.1750	10.294

Optical rotation  $[\alpha]_D = 15.47^\circ$ .

*Bornyl Chloride (Pinene Hydrochloride), C<sub>10</sub>H<sub>17</sub>Cl.*

For this and the following derivatives of this class, I am indebted to Professor Tilden. This product was made from American turpentine. Being a solid, it was examined in solution in carbon tetrachloride; two different solutions were employed.

Solution 1.—This contained 68.271 per cent. of C<sub>10</sub>H<sub>16</sub>.HCl, and had the composition C<sub>10</sub>H<sub>16</sub>.HCl + 0.523 mol. CCl<sub>4</sub>.

Density:  $d$  15°/15°, 1.1493;  $d$  20°/20°, 1.1454;  $d$  25°/25°, 1.1415.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
17.4°	1.1835	14.503
Less 0.523 mol. CCl <sub>4</sub> .....		3.442
		<hr/> 11.061

Optical rotation  $[\alpha]_D = +6.92^\circ$ .

Solution 2.—This contained 68.40 per cent. of C<sub>10</sub>H<sub>16</sub>.HCl, and had the composition C<sub>10</sub>H<sub>16</sub>.HCl + 0.517 mol. CCl<sub>4</sub>.

Density:  $d$  15°/15°, 1.1471;  $d$  20°/20°, 1.1430;  $d$  25°/25°, 1.1393.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
14.8	1.1868	14.449
Less 0.517 mol. CCl <sub>4</sub> .....		3.396
		<hr/> 11.055

Average of both determinations ..... 11.058

*Dipentene Dihydrochloride, C<sub>10</sub>H<sub>16</sub>.2HCl.*

This was examined in the fused condition. F. p. 50°.

Density:  $d$  45°/45°, 1.0613;  $d$  50°/50°, 1.0593;  $d$  55°/55°, 1.0575.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
54.8°	1.1942	13.111

*Camphene, C<sub>10</sub>H<sub>16</sub>.*

This was obtained from Schuchardt, and purified by pressure and five fractionations; it boiled at 157—157.5° under 750 mm. It was examined in the fused condition.

Density:  $d$  40°/40°, 0.8609;  $d$  45°/45°, 0.8586;  $d$  50°/50°, 0.8565;  $d$  55°/55°, 0.8544;  $d$  60°/60°, 0.8524.

Magnetic rotation :

t.	Sp. rot.	Mol. rot.
45.8°	1.1516	10.136

*Refractive Values.*

The refractive values of borneol and camphor and its derivatives were determined. The measurements were made with the same ethylene chloride solutions as were used for the magnetic rotations. It is thought to be unnecessary to give all the details of the indices, &c., determined, the molecular refractions of the compounds calculated from them being sufficient. The values obtained with these solutions would be expected generally to be very slightly lower than the pure substances would give.

The measurements of the ethylene chloride used gave the following numbers :

	$\mu$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d} \rho$	Calc.
$\alpha$	1.44758	0.35285	34.93	34.94
$\beta$	1.45607	0.35955	35.56	—
$\gamma$	1.46124	0.36363	35.99	—

$$H_{\gamma} - H_{\alpha} 1.06.$$

	$\frac{\mu-1}{d} \rho$			Disp. $H_{\gamma} - H_{\alpha}$
	$\alpha$	$\beta$	$\gamma$	
Borneol.....	75.791	77.175	77.913	2.122
Calc. ....	76.200			
Diff. ....	-0.409			
Camphor .....	74.354	75.690	76.517	2.163
Calc. ....	74.200			
Diff. ....	+0.154			
$\alpha$ -Nitrocamphor .....	84.205	85.955	86.991	2.786
Calc. ....	84.250			
Diff. ....	-0.045			
$\alpha\alpha'$ -Chloronitrocamphor .....	92.298	94.167	95.280	2.982
Calc. ....	92.820			
Diff. ....	-0.522			
$\alpha\alpha$ -Bromonitrocamphor .....	97.572	99.711	100.982	3.410
Calc. ....	98.340			
Diff. ....	-0.768			



	$\frac{\mu-1}{d} \rho.$			Disp. $H_{\gamma} - H_{\alpha}.$
	$\alpha.$	$\beta.$	$\gamma.$	
Camphoryloxime .....	85.017	86.845	87.912	2.895
Calc. ....	84.205			
Diff. ....	+0.812			
$\alpha$ -Chlorocamphor .....	82.620	84.183	85.046	2.426
Calc. ....	82.770			
Diff. ....	-0.150			
$\alpha$ -Bromocamphor .....	88.083	89.870	90.919	2.836
Calc. ....	88.290			
Diff. ....	-0.207			
$\alpha\alpha$ -Dibromocamphor .....	101.944	104.131	105.564	3.620
Calc. ....	102.380			
Diff. ....	-0.436			
$\alpha\beta$ -Dibromocamphor .....	101.572	103.633	104.988	3.416
Calc. ....	102.380			
Diff. ....	-0.808			
$\alpha\beta$ -Dibromo- $\alpha$ -chlorocamphor .....	110.391	112.851	114.276	3.885
Calc. ....	110.950			
Diff. ....	-0.560			

### XXXII.—*A Modification of Zeisel's Method for the Estimation of Methoxyl Groups.*

By J. T. HEWITT and T. S. MOORE.

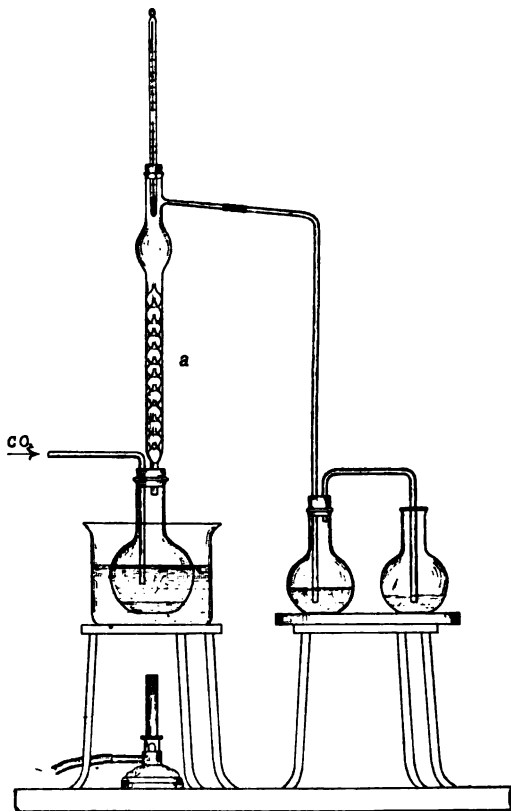
THE method described by Zeisel for the estimation of methoxyl (and ethoxyl) groups in organic compounds has frequently proved of considerable service. A disadvantage of this method is, however, the time taken both in setting up the apparatus and in carrying out the estimation. With the view of improving the process in this respect, we determined, if possible, to replace the condenser of the original apparatus due to Zeisel by a fractionating column, and this proved so satisfactory that we were able to dispense, not only with the condenser and the supply of water at constant temperature, but also with the potash-bulbs containing water with red phosphorus in suspension kept

at 40—50°. An efficient column not only returns the hydriodic acid to the decomposition flask, but also effectually holds back any iodine which volatilises.

The apparatus we have used takes the form shown in the accompanying figure, the arrangement of the bulbs in the fractionating column being shown at (a).

Carbon dioxide is washed by silver nitrate solution and led into the decomposition flask; not simply into the neck as in Zeisel's method. An ordinary round-bottomed flask of 150—200 c.c. capacity is employed, the inlet tube for carbon dioxide terminating about 1.5—2 cm. above the surface of the liquid. A fractionating column also passes through the cork of the flask, the pattern of the one we have used being due to Mr. J. N. Tervet of this laboratory. The number of bulbs in the column has been seven or eight.

The method of procedure is as follows: About 16 c.c. of hydriodic acid (sp. gr. 1.68—1.70) is poured into the decomposition flask. This is fitted with the cork carrying the carbon dioxide leading tube and the fractionating column. The bulb of the flask is then immersed in a glycerine bath and heated at about 130°, whilst a slow current of carbon dioxide is passed through the apparatus for 10 minutes.\* The apparatus is then disconnected, the flask and its contents cooled, and about 0.2—0.3 gram of the substance under



\* In this manner, impurities (for example, phosphine) are removed from the hydriodic acid. We do not know if this precaution has been previously employed.

examination weighed into it. The apparatus is then joined together again, and the tube from the fractionating column connected to one passing directly into an aqueous alcoholic solution of silver nitrate prepared according to Zeisel's directions. A further check flask is also added, as Zeisel recommends.

The decomposition flask and its contents are heated at  $130^{\circ}$ , and a slow current of carbon dioxide passed through the apparatus. Satisfactory results are obtained if during the operation the thermometer at the top of the column indicates a temperature of  $20-25^{\circ}$ . Decomposition is complete in 45 minutes (maximum time).

The following results demonstrate the satisfactory nature of the method :

Substance.	Formula.	Weight taken.	AgI produced.	CH <sub>3</sub> O found.	CH <sub>3</sub> O calculated.
Blank .....	—	—	none	—	—
Brucine .....	$C_{27}H_{39}O_5N_2(OCH_3)_2$	0.2196	0.2581	15.50	15.74
Vanillin .....	$C_8H_8(OH)(OCH_3)(CHO)$	0.2338	0.3598	20.30	20.39
Codeine * .....	$C_{17}H_{19}ON(OH)(OCH_3)$	0.3917	0.2674	9.05	10.35
Quinine .....	$C_{20}H_{21}ON_2(OCH_3)$	0.2745	0.2191	10.52	10.35
		0.2055	0.1432	9.51	9.56

\* The codeine reacidified on treatment with hydriodic acid. In the second estimation, the substance was heated with hydriodic acid mixed with about its own volume of acetic anhydride.

The method generally giving such good results, attempts were made to estimate methoxyl in easily volatile substances. The results were not very satisfactory :

Substance.	Formula.	Weight taken.	AgI produced.	CH <sub>3</sub> O found.	CH <sub>3</sub> O calculated.
Methyl acetate ...	$CH_3 \cdot CO_2CH_3$	0.2159	0.5142	31.41	41.89
Methyl oxalate ...	$CO_2CH_3$ $ $ $CO_2CH_3$	0.2207	0.8492	50.75	52.54

For ethoxyl compounds, the glycerine bath is heated at  $140^{\circ}$ , and the current of carbon dioxide is made somewhat more rapid towards the end of the operation. The temperature at the top of the fractionating column is about  $27^{\circ}$  :

Substance.	Formula.	Weight taken.	AgI produced.	C <sub>2</sub> H <sub>5</sub> O found.	C <sub>2</sub> H <sub>5</sub> O calculated.
<i>m</i> -Chlorobenzene-azo- <i>p</i> -phenetole	C <sub>6</sub> H <sub>4</sub> Cl·N <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·OC <sub>2</sub> H <sub>5</sub>	0·2560	0·2304	17·23	17·54

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### XXXIII.—*The Radioactivity of Thorium Compounds. I.* *An Investigation of the Radioactive Emanation.*

By E. RUTHERFORD, M.A., D.Sc., Macdonald Professor of Physics,  
 and FREDERICK SODDY, B.A. (Oxon.), Demonstrator in Chemistry,  
 McGill University, Montreal.

THE following paper contains a preliminary account of an investigation into the property possessed by the compounds of thorium of giving a radioactive emanation, and also into the nature of the emanation itself.

It was shown by one of us (*Phil. Mag.*, 1900, [v], 49, 1, 161) that the compounds of thorium, besides being radioactive in the same sense as the uranium compounds, also continuously emit into the surrounding atmosphere, under ordinary conditions, something which, whatever its real nature may be, behaves in all respects like a radioactive gas. This "emanation," as it has been named, is the source of rays, which, like the Röntgen and uranium rays, and the ordinary well-recognised type of thorium radiation, will darken a photographic plate, and will render a gas capable of conducting an electric current (that is, will "ionise" it), but is sharply distinguished from them by the following considerations. It can be moved from the neighbourhood of the thorium compound by a current of air passing over it, or even by the process of ordinary gaseous diffusion, and transported long distances, so that the characteristic photographic and ionisation effects appear in the air far away from the original source of radioactivity. The Röntgen and uranium rays, as is well known, travel in straight lines from their source, and any object opaque to them interposed in their path will sharply screen the space behind. But in the case of the thorium radiation there is no such screening effect, because here we have a case of a substance emitting, not only straight line radiation, but also particles of a gas, itself radioactive, capable of diffusing

through the surrounding atmosphere around obstacles placed in its direct path, and so arriving and producing its effects at points completely screened from rays travelling from the thorium in straight lines. It was shown in the original communication that these effects could not be ascribed to minute particles of thorium dust carried off mechanically, and all the subsequent work on the subject shows that the hypothesis that the compounds of thorium emit a radioactive gas is not merely the only one which will explain the facts, but that it does so in every observed case in a completely satisfactory manner.

*Present State of the Subject from a Physical Standpoint.*

In the papers referred to, the general character of the phenomena in question was presented, and a short *résumé* will perhaps not be out of place here. It was shown that the radiation from the emanation decays rapidly, but at a perfectly defined rate, that is, the effects it produces diminish with the lapse of time, falling to about one-half the original value at the end of one minute. This "rate of decay," as will be shown later, is of great value in identifying and distinguishing between different types of emanation.

The emanation passes unchanged through cotton wool, weak and strong sulphuric acid, and aluminium and other metals in the form of foil, but not through an extremely thin sheet of mica.

The emanating power of thorium is independent of the surrounding atmosphere, but is destroyed to a large extent by intense ignition, and does not return when the substance is kept.

One of the most striking properties of the thorium emanation is its power of exciting radioactivity on all surfaces with which it comes in contact, that is, a substance after being exposed for some time in the presence of the emanation behaves as if it were covered with an invisible layer of an intensely radioactive material. If the thorium is exposed in a strong electric field, the excited radioactivity is entirely confined to the negatively charged surface. In this way, it is possible to concentrate the excited radioactivity on a very small area. The excited radioactivity itself has a regular rate of decay, but different from that of the emanation, its effect falling to half value in about 11 hours. There is a very close connection between the excited radioactivity and the emanation. It was shown that the amount of the former produced under various conditions was proportional to the amount of the latter, and if the emanating power of thorium be destroyed by intense ignition, its power to excite radioactivity correspondingly disappears. Some apparent discrepancies which at first stood in the way of too close a connection being inferred have resolved

themselves by recent work into strong confirmation of the view that the two are related to each other as cause and effect.

Another remarkable property of the excited radioactivity is that it is soluble in sulphuric and hydrochloric acids, that is, a platinum wire, rendered radioactive by being made the negative pole of an electric field in the neighbourhood of some thorium, will give up its radioactivity to these acids. If the acid be then evaporated, the radioactivity remains on the dish, whilst if left to itself the radioactivity of the acid solution decays at a rate identical with that of the original excited radioactivity on the platinum wire.

Simultaneously with the discovery of excited radioactivity due to thorium, Curie showed that radioactive barium possessed a similar property. Later, Dorn (*Abh. der Naturforsch. Ges. für Halle-a-S.*, 1900) repeated the work quoted for thorium, and extended it to include two preparations of radioactive barium compounds (radium) prepared by P. de Haen, and a preparation of radioactive bismuth (polonium). He found that radium gave out an emanation which was similar to that from thorium, but which retained its radioactive power much longer. The excited radioactivity from radium, on the other hand, decayed more rapidly than that from thorium. The special property of emitting an emanation is, however, confined to the compounds of radium and thorium, those of uranium and polonium do not possess it to an appreciable extent.

An approximate determination of the molecular weight of the emanation produced by radium has been carried out (Rutherford and H. T. Brooks, *Nature*, 1901, 64, 157) by a diffusion method, taking advantage of the slow rate of decay of the radium emanation. From comparison of the rate of diffusion of gases of known molecular weight into one another, it was found that the molecular weight probably lies between 40 and 100.

It seemed probable that an examination of the phenomena by chemical methods might throw light upon its nature, and the emanation produced by thorium was chosen as more suitable for the purpose than that produced by radium, on account of the obscurity still surrounding the chemistry of the latter, and the difficulty of producing material of even approximate uniformity of properties. Thorium, on the other hand, is an article of commerce, and specimens from different sources show surprising uniformity in this respect.

During the progress of the work, the subject has acquired additional importance and interest through the discovery by Elster and Geitel (*Phys. Zeit.*, 1901, 2, 590) that it is possible to produce excited radioactivity from the atmosphere, without further agency, by simply exposing a wire highly charged to a negative potential in the atmosphere for many hours, and that this also possesses the property of

being dissolved off by acids, and of being left behind unchanged on the evaporation of the latter. But here again the rate of decay is different from that of the excited radioactivity produced by thoria, which is evidence for assuming that the two are probably not identical, although so strikingly analogous. However, the close connection between excited radioactivity and the emanation established in the case of thoria renders it probable that the excited radioactivity obtained from the atmosphere is caused by the presence there of an emanation or radioactive gas analogous to, although probably different from, the Thorium emanation. The discovery is likely, as Elster and Geitel point out, to have important bearings on the theory of atmospheric electricity, and in our opinion renders a close study of the thorium emanation the more imperative.

#### *The Chemical Aspect of the Question.*

The foregoing furnishes a short review of the physical side of the question at the present time. With regard to the chemical aspect, this has so far not been studied. The photographic method, almost the only one that has until now been used by chemists in the study of radioactivity, is not one which allows of the recognition and differentiation of an emanation as a component factor in producing the phenomena. The photographic method is of a qualitative rather than a quantitative character ; its effects are cumulative with time, and as a rule long exposures are necessary when the radioactivity of a feeble agent like thoria is to be demonstrated. In addition, Russell has shown that the darkening of a photographic plate is brought about also by agents of a totally different character from those under consideration, and, moreover, under very general conditions. Sir William Crookes (*Proc. Roy. Soc.*, 1900, 66, 409) has sounded a timely note of warning against putting too much confidence in the indications of the photographic method of measuring radioactivity. The uncertainty of an effect produced by cumulative action over long periods of time quite precludes its use for work of anything but a qualitative character.

Two or three chemists have studied the radioactivity of thoria, using the photographic method, without, however, distinguishing between the radioactivity due to the emanation and that due to the thoria itself. Sir William Crookes (*loc. cit.*), who succeeded by an elegant method in separating and isolating the radioactive constituent of uranium, also describes some experiments on thorium compounds with the same object, but did not succeed in effecting a separation. A method based on the fractional precipitation of the sulphate failed completely, but another method, the fractional crystallisation of the nitrate, gave pre-

parations showing a difference in their photographic actions in the ratio of one to three. According to slight variations in the method employed, as, for example, whether a glass or a card bottom was used for the cell containing the substance to be tested (and both seem to have been employed), the radiation from the emanation would or would not contribute largely to the photographic action observed.

Debiegne (*Compt. rend.*, 1900, 130, 906), working on a very large scale, obtained from pitchblende, by using reactions which would lead to the separation of thorium, a material different in its chemical properties from radium (barium) and polonium (bismuth), but consisting in great part of thorium. This preparation was 100,000 times more active than uranium, and he therefore assumed the existence of a new element, "actinium," therein. He hazarded the suggestion that the radioactivity of thoria is due to the presence of the same substance, and derived support for this view from the recent work of one of us on the radioactivity of thoria, although on what grounds is not clear.

In the course of their work on the atomic weight of thorium, Brauner (*Trans.*, 1898, 73, 951) and Baskerville (*J. Amer. Chem. Soc.*, 1901, 23, 761), have obtained evidence of the presence of a foreign substance associated with thorium. The latter noticed that the separation, as he interpreted it, of this impurity reduced the photographic action considerably, and he concluded that the pure material would be without photographic action. He employed a modification of Crookes' photographic method, but it cannot be decided with certainty from the description whether the radiation from the emanation would be eliminated or not.

The present work is concerned primarily with the radioactive emanation, although, of course, frequent occasion has arisen to examine correspondingly the ordinary radiation also. The methods employed are of an electrical character, based on the property generally possessed by all radiation of the kind in question, of rendering a gas capable of discharging both positive and negative electricity. These, as will be shown, are capable of great refinement and certainty. An ordinary quadrant electrometer is capable of detecting and measuring a difference of potential of at least  $10^{-2}$  volts. With special instruments, this sensitiveness may be increased a hundredfold. An average value for the capacity of the electrometer and connections is  $3 \times 10^{-5}$  microfarads, and when this is charged up to  $10^{-2}$  volts, a quantity of electricity corresponding to  $3 \times 10^{-13}$  coulombs is stored up. Now in the electrolysis of water one gram of hydrogen carries a charge of  $10^5$  coulombs. Assuming, for the sake of example, that the conduction of electricity in gases is analogous to that in liquids, this amount of electricity corresponds to the transport of a mass of  $3 \times 10^{-18}$  grams.



of hydrogen, that is, a quantity of the order of  $10^{-12}$  times that detected by the balance. For a more delicate instrument, this amount would produce an inconveniently large effect.

The effects under investigation, from the nature of their manifestation, may well be, and probably are, produced by quantities of matter of the order of magnitude described, and therefore altogether beyond the range of the balance. But to assume on that account that the subject is beyond the pale of profitable chemical investigation is needlessly to limit the field of chemical inquiry. Although surpassing the spectroscope as a detective agent, as a quantitative instrument the electrometer is little inferior in accuracy to the balance. To take as an example the case of thorium mixed with zirconia, the former could be detected and accurately measured by means of its emanation with an electrometer, even although it were only present to the extent of one part in many thousands. A distinction must be made here between *emanation* and *emanating power*. The quantity of the former is what is measured by the electrometer. To express this in terms of weight, the emanating power, that is, the quantity of emanation produced by a given weight of the substance in question, must be known. As will be shown, this value varies with the previous history and present condition of the substance.

The electrometer also affords the means of recognising and differentiating between the emanations of different chemical substances. By the rate of decay, the emanation from thorium, for example, can be instantly distinguished from that produced by radium, and although a difference in the rate of decay does not of itself argue a fundamental difference of nature, the identity of the rate of decay furnishes at least strong presumption of identity of nature.

In the sense that has just been explained, the electrometer can be said to supply the investigation of the property of emanation with methods, so to speak, of quantitative and qualitative analysis which are simple and direct, and there is therefore no reason why the property in question, and even the nature of the emanation itself, should not be the subject of chemical investigation.

### *Scope of Work.*

Of the great number of questions which immediately present themselves for answer in an investigation of this kind, the following are at present claiming our more immediate attention.

1. Is the power of producing an emanation a specific property of thorium, or is it to be ascribed to the presence of a foreign substance, possibly in minute amount, associated with it and amenable to chemical methods of separation?

2. Can the emanating power of "de-emanated" thorium be regenerated by chemical means? It has been mentioned that thorium, when intensely ignited, loses to a very great extent its power of giving an emanation. If such de-emanated thorium be subjected to a series of chemical changes, will it regain its emanating power or not?

3. Does the emanation or radioactive gas itself possess any property which would associate it chemically with any known kind of gravitational matter?

4. Is it possible to detect, by means of the balance, any loss in weight corresponding to the continuous emission of the emanation or any gain in weight of bodies rendered radioactive thereby?

5. Does the chemistry of thorium present any peculiarity capable of being connected with its almost unique power of producing an emanation?

To interpret rightly the results obtained, a more or less complete study of the effect of chemical and physical conditions on the emanating power is necessary. The effect of the state of aggregation, the presence or absence of water, the influence of light, temperature, the nature of the surrounding atmosphere, the lapse of time since preparation, &c., on the emanating power, as well as the differences in this property exhibited by different compounds, have been investigated.

The present communication does not attempt a full answer to all the above questions. The results so far obtained in answer to the first three will be presented. The work on the fourth is in progress, whilst the results of the investigation of the fifth question will be most conveniently given later in a separate communication.

#### *Electrometer Method of measuring Emanating Power and Radioactivity.*

The term radioactive is now generally applied to a class of substances, like uranium, thorium, radium, and polonium, which have the power of spontaneously giving off radiations capable of passing through thin plates of metal. The radiations are in some cases very complex, but in the case of the substances mentioned, a portion at least of the radiation is similar in all respects to easily absorbed Röntgen rays. The characteristic and general property possessed by these radiations is to produce, from the gas through which they pass, positively and negatively charged carriers, which in an electric field travel to the negative and positive electrodes respectively. In this way, a small current is able to pass through a gas exposed to the radiations, even with a very weak electric field, and the measurement of this current by means of the electrometer affords a means of comparing the intensities of radiation.

As has been mentioned, compounds of thorium (and radium), in

addition to radiations which travel in straight lines, emit radioactive emanations, which behave in all respects like a temporarily radioactive gas, and diffuse rapidly through porous substances, as, for example, thick cardboard, which are completely opaque to straight line radiation. Each particle of the emanation behaves as if it were a radiating centre, producing charged carriers throughout the gas in its neighbourhood. The emanation passes through plugs of cotton wool and can be bubbled through liquids without appreciable loss of radioactivity, whereas the charged carriers, produced by the emanation in common with the straight line radiation from radioactive substances, on the contrary, completely disappear on passing through a plug of cotton or glass wool, or by bubbling through liquids. The means of eliminating the effects of the straight line radiation and of measuring the amount of the emanation alone thus suggest themselves. Air passed over uranium or other non-emanating radioactive substance will no longer conduct a current after passage through cotton wool. The conductivity in the case of thorium, however, will persist, and afford a measure of the amount of emanation present.

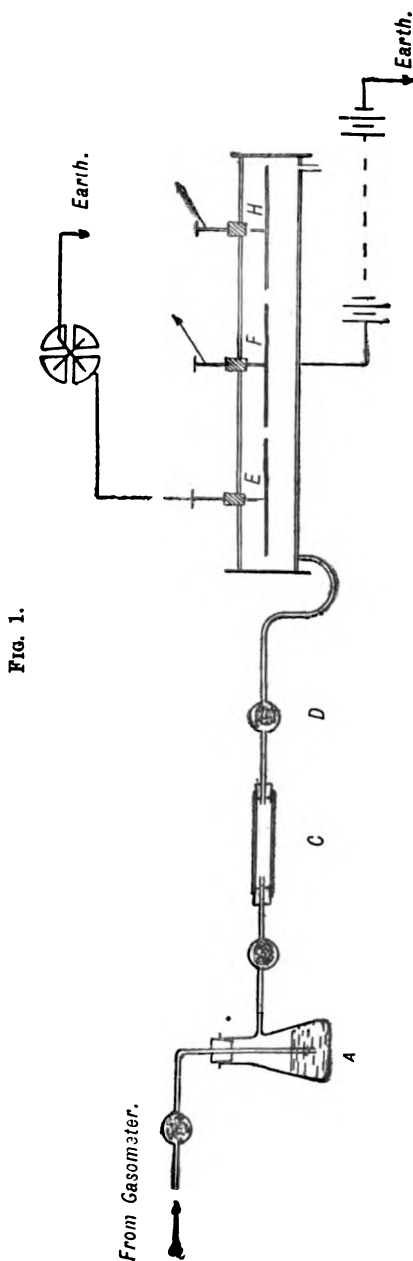
Fig. 1 shows the experimental arrangement for comparing the emanating power of substances. These are placed in the form of fine powder in a shallow lead vessel inside the glass cylinder, *C*, 17 cm. in length and 3.25 cm. in diameter, provided with indiarubber corks. A current of air from a large gas-bag, after passing through a tube containing cotton wool to remove dust particles, bubbled through sulphuric acid in the vessel, *A*. It then passed through a bulb containing tightly packed cotton wool to prevent any spray being carried over. The emanation mixed with air was carried from the vessel *C* through a plug of cotton wool, *D*, which completely removed all the charged carriers carried with the emanation. The latter then passed into a long, brass cylinder, 75 cm. in length and 6 cm. in diameter. The cylinder insulated on paraffin blocks was connected to one pole of a battery of small lead accumulators, the other pole of which was connected to earth. Three electrodes, *E*, *F*, *H*, of equal length were placed along the axis of the cylinder, supported by brass rods passing through ebonite corks in the side of the cylinder. The current through the gas, due to the presence of the emanation, was measured by means of a Kelvin quadrant electrometer of the White pattern. The electrometer and the connections were suitably screened by means of wire gauze connected to earth. An insulating key was arranged so that either of the electrodes *E*, *F*, *H*, or all of them together, could be rapidly connected to one pair of quadrants of the electrometer, the other two being always connected to earth.

The insulation of the electrodes was first tested by sending a current of air through the apparatus without any emanating material in *C*,

The rate of movement of the electrometer needle was accurately observed. On placing the emanating substance in *C* and continuing the air current for several minutes at a constant rate, the current due to the emanation reached a steady state. On separating the quadrants of the electrometer, the deflection from zero increased uniformly with time. The time taken to pass over 100 divisions of the scale was observed with a stop-watch. The number of divisions passed over per second may be taken as a measure of the current through the gas.

With this apparatus, the emanation from 10 grams of ordinary thorium oxide produces a current of  $3.3 \times 10^{-11}$  amperes between the three electrodes connected together and the cylinder. With the electrometer working at average sensitiveness, this corresponded to a deflection of 100 divisions of the scale in 12 seconds, so that one-hundredth part of this current could be readily measured, that is, the emanation produced by one-tenth of a gram of thorium oxide.

An electrometer one hundred times more sensitive than this failed to detect the presence of an emanation or radioactivity in the oxides of tin, zirconium, and titanium, the other elements of the same group in the periodic table.



*Variation of the Current with Voltage.*—The current through the gas observed with the electrometer at first increases with the voltage, but a stage is soon reached when there is a very small increase for a large additional voltage. This is one of the most characteristic properties of conducting gases. For small voltages, only a small proportion of the charged carriers reach the electrode, on account of their recombination throughout the volume of the gas. When the electric field is increased until all the carriers reach the electrode before any appreciable recombination can occur, the current is at a maximum, and remains constant for large increases of voltage, provided, of course, that the electric field is below the value necessary for a spark to pass. In the experimental case, a pressure of 50 volts was found sufficient to give the maximum current between the electrodes.

This property of conducting gases allows us at once to make sure that the insulation of the electrodes is perfect at all stages of a long experiment; 100 volts applied instead of 50 to the cylinder should give the same current if the insulation is unaffected.

*Rate of Decay of the Radiation from the Emanation.*—The three electrodes, *E*, *F*, *H*, were used to compare the "rates of decay" of the radiations from the emanations of different substances. In the previous papers quoted, it has been shown that the radiating power of the thoria emanation falls to half its value in about a minute. In consequence of this, the current observed for the electrode *E* is greater than for electrode, *H*. Knowing the velocity of the current of air along the cylinder and the respective currents to the electrodes *E*, *F*, *H*, the rate of decay of the radiation can be readily deduced. If, however, we merely require to compare the rate of decay of one emanation with another, it is only necessary to compare the ratio of the currents to the electrodes *E*, *F*, *H* in each case, keeping the current of air constant. If the ratio of the currents is the same we may conclude that the radiating power of each diminishes at the same rate. The comparison of emanation is thus rendered qualitative as well as quantitative. In most of the experiments, the current to the electrode *E*, was about twice that to the electrode *H*; the velocity of the current of air along the cylinder was thus about 0.8 cm. a second.

*Comparison of Emanating Power.*—The experiments in all cases on the amount of emanation from different substances are comparative. The standard of comparison was usually a sample of 10 grams of thoria as obtained from the maker, which gave out a conveniently measurable quantity of emanation. Preliminary experiments were made to find the connection between the weight of thoria and the amount of emanation as tested in the cylinder. The following

numbers show that the amount of emanation is directly proportional to the weight of the substance :

Weight of thoria.	Divisions of scale per second.
2 grams.	1.41
4     "	2.43
10    "	6.33
20    "	13.2

This result shows that within the limit of accuracy desired we may take the amount of emanation as directly proportional to the weight of the substance. The determinations in the above table were made with the three electrodes connected together with the electrometer, and with a constant flow of air. The lead vessel in which the thoria was placed was 7.4 by 3.5 cm. in area and 3 mm. deep. In the comparison of emanating power, the maximum current between the electrodes for the standard 10 grams of thoria was first observed. This was removed and a known weight of the specimen to be tested was substituted, and the deflections again observed after the conditions had become steady.

If  $d_1$  = No. of divisions per sec. for a weight,  $w_1$ , of thoria ;  
 $d_2$  =                   "                   "                    $w_2$ , of the specimen ;  
 then

$$\frac{\text{Emanating power of specimen}}{\text{Emanating power of thoria}} = \frac{d_2 w_1}{d_1 w_2}.$$

The values  $d_1$  and  $d_2$  are corrected, when necessary, for natural leakage, that is, the current which passes under similar circumstances when no emanating material is present. This current is chiefly made up of a leakage due to conduction over the ebonite, as well as the current produced by the excited radioactivity which has collected on the negative electrode during the course of the day's experiments. It is generally very small, and the correction is only necessary when a specimen of substance almost free of emanation is being tested.

An example taken at random from the note-book will serve to illustrate the method of calculating the results, the emanating power of the comparison sample being considered 100 per cent. :

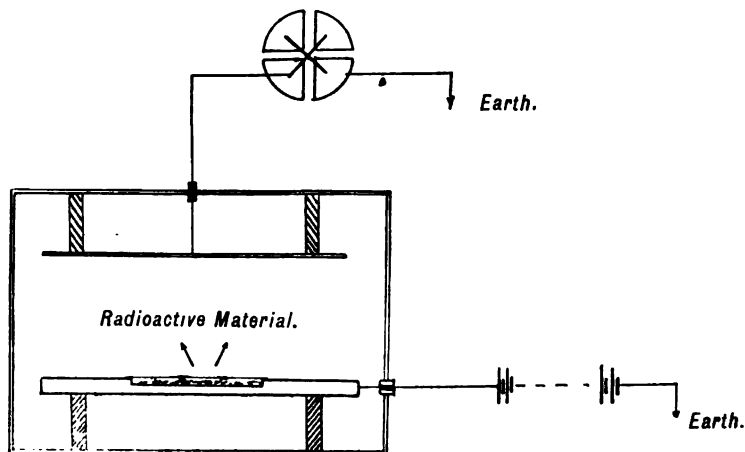
Dec. 7th, 11 a.m.—Natural leakage .....	10 divisions in 50"
	0.20     "     1"
5 grams comparison sample $\text{ThO}_2$ .....	100     "     23.5"
3.6   " $\text{ThO}_2$ ignited 24 hours over	
Bunsen burner in platinum crucible	50     "     35.2"
$d_1 = 4.25$ , corrected for nat. leakage = .....	4.05
$d_2 = 1.42 =$ .....	1.22
$\frac{d_2 w_1}{d_1 w_2} =$	0.42, or 42 per cent.

*Comparison of Intensity of Straight Line Radiation.*

It was frequently of interest to obtain information about the intensity of the ordinary radiation correspondingly with measurement of emanating power. In order to do this rapidly and accurately, the following method was used. Fig. 2 shows the general arrangement. 0.1 gram of the compound to be tested was reduced to fine powder and uniformly sifted over a platinum plate 36 sq. cm. in area.

This plate was placed on a large metal plate connected to one pole of a battery of 300 volts, the other pole of which was earthed. An insulated parallel plate was placed about 6 cm. above it, and the whole apparatus enclosed in a metal box connected to earth, to prevent electrostatic disturbance. The shaded portions in the figure represented

FIG. 2.



insulators. A door was made in the apparatus so that the plate could be rapidly placed in position or removed. The current between the plates is observed in the usual way with the electrometer. The ratio of the currents for two substances is a comparative measure of their radioactivity. It is only possible to compare together with certainty substances of similar density and state of division,—a light, floury material will tend to give lower values than a dense powder.

If a substance gives off an emanation, the current between the plates increases with time. Under these conditions when the thorium is exposed in thin layers with a maximum of radiating surface, all but 1 or 2 per cent. of the total effect is due to the straight line radiation; even when the effect due to the emanation has attained its

maximum, this constitutes a very small percentage of the whole. This effect, however, may be to a large extent eliminated by taking the current between the electrodes immediately after the material is placed in the testing apparatus, or by passing a current of air between the electrodes to remove the emanation, and prevent it accumulating.

It is thus possible to compare intensity of radiations with an error not exceeding 1 or 2 per cent., and with great rapidity, and in these respects the electrical method is altogether superior to the photographic.

*Comparison of Emanating Power.*—The apparatus (Fig. 2) described for the comparison of radiations, can also be quite well employed for a comparison of emanating power. In this case, a thick layer of thoria (several grams) is spread over the plate and covered with two thicknesses of ordinary paper. This has been found almost completely to stop the straight line radiation, whilst allowing the emanation to pass through unimpeded. The current is now measured when a steady state has been reached, due to the accumulation of the emanation. This takes some time, and draughts of air must be guarded against. For this reason, it is less convenient than the method first described, but the results obtained by the two methods are almost exactly the same. Thus a sample of "de-emanated" thoria which gave 12 per cent. of the emanating power of the comparison sample by the first method gave 13 per cent. by the second method, whilst a sample of oxide prepared from thorium oxalate gave 37 per cent. and 39 per cent. by the two methods respectively. The close agreement in the values by methods so completely different in character is a proof that the indications of the methods are worthy of a great degree of confidence.

#### *The De-emanation of Thoria and the Regeneration of the Emanating Power.*

The emanating power of thoria, as has been stated, is destroyed to a large extent by intense ignition. A closer study of this is the first step in the investigation of the phenomenon. Previous experiments had not succeeded in completely de-emanating thoria, although a reduction to about 15 per cent. of its original value had been accomplished. A sample of this preparation which had been kept for two years had not altered from this value. An experiment was performed in which thoria was heated to the highest temperature which could be safely employed with platinum vessels: (1) in a thin layer in a large platinum dish, and (2) in bulk in a small platinum crucible placed inside the dish. The two were heated together by



means of a powerful gasoline furnace for one hour. The temperature was such that the fireclay walls fused, and the pipeclay of a triangle showed signs of having been softened. It was found that the sample that had been heated in a thin layer in the dish retained about 16 per cent. of its original emanating power, whilst the other sample retained about 8 per cent. There is thus no advantage in heating in thin layers, in fact rather the reverse, for the sample showing 16 per cent. again heated to a slightly lower temperature for half-an-hour in a small crucible was reduced to 12 per cent.

In another experiment, a small platinum crucible filled with thoria was heated for half-an-hour in a small furnace by a large blowpipe and powerful pair of bellows. Some asbestos wool had completely fused on the outside of the crucible, and the temperature was probably but little lower than in the previous experiment. This sample also retained about 8 per cent. of its emanating power. No further attempt has yet been made to completely destroy the emanating power.

A small quantity of thoria heated in a platinum crucible in the open over an ordinary small sized blowpipe and bellows for five minutes retained about 45 per cent. of its emanating power. The effect of time as well as of temperature was studied by heating about equal quantities in a platinum crucible over an ordinary Bunsen burner for different periods.

Heated 10 minutes	Emanating power = 61 per cent.
„ 1 hour	„ = 59 „
„ 24 hours	„ = 42 „

It thus appears that there is a large and practically sudden decrease of emanating power for each temperature above a red heat, followed by a very gradual decrease with time when the temperature is maintained; thus five minutes on the blowpipe, whilst much more effective than the same time at the temperature of the Bunsen burner, produced rather less effect than 24 hours at the latter temperature.

*Effect of Moisture.*—The next point to be examined was whether the loss of emanating power could be attributed to a loss of water and desiccation of the thoria by ignition. A sample of de-emanated thoria (retaining about 14 per cent.) was placed in the middle of a Jena glass tube, one end of which was closed and contained water, the other end being drawn out to a jet. This was supported in a powerful tube furnace in a sloping position, and the part containing the thoria heated to the highest possible temperature, while a slow current of steam from the water at the end was passed over it, escaping by the jet. When all the water had evaporated, the jet was drawn off and the tube allowed to cool in an atmosphere of steam free from air.

The thoria, on testing, was found to have been lowered in emanating power to about 7 per cent. The further heating had thus reduced the emanating power without the steam having at all regenerated it.

In the next experiment, the reverse process was tried. Two exactly parallel processes were carried out for ordinary thoria possessing the normal amount of emanating power. In the first, it was heated in a porcelain tube in the tube furnace for three hours, while about 500 c.c. of water were distilled over it from a retort. In the second, another quantity of thoria was heated in exactly the same way for the same time, only a current of well dried air was substituted for the steam. The result was conclusive: each sample had had its emanating power reduced to exactly the same amount, that is, about 50 per cent. of the original.

These experiments prove that water vapour exerts no influence either in de-emanating thoria or in effecting a recovery of its lost emanating power.

*The Regeneration of the Emanating Power by Chemical Processes.*—The task of subjecting de-emanated thoria to a series of chemical changes to see if it would recover its lost emanating power was then undertaken.

It may first be mentioned that thoria which has been subjected to ignition has changed very materially in chemical and physical properties. The pure white colour changes at temperatures corresponding to the first stages of de-emanation to a light brown, and after subjection to the very highest temperatures to a pure pink. At the same time, as has been observed before, the solubility of the substance in sulphuric acid is greatly diminished. A part always obstinately refuses to dissolve, even after long and repeated boiling with the concentrated acid, although this part is diminished by each successive treatment and appears to be in no way different from the rest of the substance. No difference, however, occurs in the readiness with which chlorine attacks it when intimately mixed with carbon. The formation of the chloride by this method is the easiest way of dissolving ignited thoria.

Two quantities of the same de-emanated thoria were converted, the one into chloride and the other into sulphate, by the usual methods, and from each of these the oxalate was formed by precipitation of the acid solution with oxalic acid. Parts of the oxalates were then converted into oxides by heating over the Bunsen burner. In both cases there was a very marked recovery in emanating power; the oxide obtained from the sulphate had about 40 per cent., that from the chloride about 55 per cent., whereas the de-emanated thoria from which they were both produced had about 13 to 14 per cent. of the emanating power of thoria. The oxalates from which the oxides

were formed each had about 11 per cent. of the power, and in converting them into oxides it was ascertained by a direct trial that too high a temperature had been employed and the thorium oxide had suffered partial de-emanation. At this time also, it was beginning to be realised that the emanating power was a quantity which varied, not only with the nature of the chemical compound, but also for the same compound very materially with its previous history. Thus the oxide from the oxalate does not possess as a rule so great an emanating power as that used for comparison, which would account for the above result. The following two exactly parallel experiments were therefore made, the one with ordinary, and the other with de-emanated thoria possessing 9 to 10 per cent. of the emanating power of the first. Each was converted to chloride in the ordinary way, by mixing with sugar solution, carbonising, and igniting the mixture of oxide and carbon so obtained in a current of dry chlorine. Each sample was then treated with water, the thorium precipitated as hydroxide with ammonia, and the hydroxides washed and dried at  $110^{\circ}$ . The hydroxide prepared from the de-emanated thoria possessed 128 per cent., that from the ordinary thoria 108 per cent. of the emanating power of ordinary thoria, when tested immediately after drying. Now a sample of hydroxide previously obtained had shown no less than three times the emanating power of ordinary thoria. The specimens were therefore tested again after having been kept for four days in loosely corked tubes. They now showed 157 per cent. and 139 per cent. respectively. The emanating power was thus increasing, so both specimens were exposed side by side in open watch glasses under a sheet of glass to keep off the dust. The result is again conclusive :

	From de-emanated $\text{ThO}_2$ .	From ordinary $\text{ThO}_2$ .
After nine days.....	253 per cent.	253 per cent.
After three more days	259     ,,	259     ,,

Thus the process of de-emanating thoria by ignition does not irretrievably destroy the emanating power, for after solution and reprecipitation no difference whatever exists in the emanating power between ordinary and de-emanated thoria.

The results also bring out another point,—the marked effect of time and exposure to air in increasing the emanating power of thorium hydroxide. This will be examined more fully later.

A fair conclusion from these experiments is that the cause of the emanating power is not removed by ignition, but only rendered for the time being inoperative.

*Radioactivity of De-emanated Thoria.*—The “straight line” radiation of thoria, de-emanated as completely as possible by ignition, was compared with that of ordinary thorium oxide by the method described.

It was found that within the limits of error no difference whatever could be detected between them. This result serves to bring out the fact that the power of thoria to give an emanation is independent of its power to give a direct radiation.

*Is the Emanating Power a Specific Property of Thorium?*

Having shown that the de-emanation of thoria by the processes described consists rather in a temporary obliteration of the effect than in a removal of the cause producing it, the next question to be considered is whether it is possible to remove from thorium compounds by chemical methods any constituent to which the property of emanating power can be traced.

The thoria used in the investigation is that supplied by Messrs. Eimer and Amend of New York, and is obtained from monazite sand by a secret process. It, of course, does not consist of pure thoria, although from superficial investigation it appears to be of excellent quality. There is a small quantity of a substance present which can be precipitated by sodium phosphate after removal of the thorium as hydroxide by ammonia, the nature of which is at present under investigation. The most noticeable impurity is about 1 per cent of thorium sulphate. Careful washing completely removed this impurity, and the emanating power of the washed sample was identical with the ordinary. The impurity may therefore be disregarded for present purposes.

Emanating power is not confined to thorium from any particular source. Orangeite and thorite from Norway both possess it as well as monazite sand from Brazil. A specimen of thoria prepared from orangeite by the ordinary processes possessed about the same emanating power as that obtained from monazite sand by the secret process.

A quantity of thorium oxide was converted into the anhydrous sulphate and dissolved in iced water. The temperature was allowed to rise and the hydrated sulphate precipitated in four fractions, a fifth being obtained by evaporation of the mother liquor to dryness. These showed no marked difference in emanating power among themselves. The first fraction was dehydrated and again submitted to fractional precipitation as hydrated sulphate. The first fraction of the new series—designated fraction AA—was then compared in the following manner with the mother liquor fraction of the first series—designated as fraction E. Both were dehydrated, dissolved in water, and precipitated as hydroxide by ammonia, washed and dried under the same conditions, and compared together at regular intervals with a comparison sample of ordinary thoria.

	Fraction AA.	Fraction E.
At first .....	203 per cent.	200 per cent.
After 1 day .....	240 „	249 „
After 13 days .....	316 „	321 „
After 43 days .....	352 „	372 „

The differences are too small to afford any indication of separation of the emanating material.

The straight line radiations of the two fractions tested in the apparatus (Fig 2) also proved to be identical.

It was obviously useless trying any further fractionations by this method. Since there was no appreciable difference in either property in the fractions tried, there was nothing to be gained in a further repetition. These results completely accord with those of Sir William Crookes (*loc. cit.*), with which, however, we were not acquainted until after our own experiments had been performed.

Another method for the purification of thoria, employed by Dennis (*J. Amer. Chem. Soc.*, 1896, 18, 947), the precipitation of the hydroxide by potassium azoimide, was next tried. The latter reagent was prepared by Thiele's method (*Annalen*, 1892, 270, 1) from diazoguanidine nitrate. Hydrazoic acid partially neutralised with potash precipitates thorium hydroxide from the boiling solution of a thorium salt. This hydroxide, compared with a sample which had been precipitated with ammonia in the ordinary way, showed similar emanating power.

These results, which fail to give any indication of a separation of the emanating material by chemical means, taken in conjunction with those already described in the preceding section on the regeneration of the emanating power in de-emanated thoria, certainly seemed to point to the conclusion that the power of giving an emanation is really a specific property of thorium. Recent results, which will be given in the last section (p. 343), put the question in a fresh light.

#### *Effect of Conditions upon Emanating Power.*

Before any further work was undertaken, it was necessary to make a close study of the influence of conditions upon the emanating power of thorium compounds.

*Effect of Temperature.*—The effect of increase of temperature on the emanating power of thoria has already been fully investigated by one of us (*Phys. Zeit.*, 1901, 2, 429). The results stated briefly show that an increase in temperature up to a certain limit, in the neighbourhood of a red heat, correspondingly increases the emanating power. At the maximum, this is between three and four times the value at the ordinary temperature, and is maintained at this increased value for

several hours without any sign of diminution with time. When the thoria is allowed to cool, the emanating power then returns to the neighbourhood of the normal value. If, however, the limit of temperature given is exceeded, de-emanation sets in, and even while the high temperature is maintained, the emanating power falls rapidly to a fraction of its former value. On cooling, the substance is found to be more or less de-emanated. It is of interest that no increase of emanating power is observed when de-emanation commences.

These experiments were extended to include the effects of cooling. The platinum tube which contained the thoria was surrounded with a felt jacket containing a mixture of solid carbon dioxide and ether. The emanating power immediately fell to 10 per cent. of its former value. On removing the cooling agent, it again rose quickly to nearly its normal value.

In another experiment, some thoria was surrounded in a platinum crucible with a mixture of solid carbon dioxide and ether, and kept in a vacuum for several hours. On removing it and allowing its temperature to rise, it possessed much the same value as an ordinary sample, and after standing some time in the air it was again tested and no difference could be detected between the two.

Thus changes in temperature produce very marked simultaneous changes in emanating power, but between the limits of  $-110^{\circ}$  and an incipient red heat no permanent alteration in the value occurs.

*Effect of Moisture.*—Dorn (*loc. cit.*) had noticed that moisture produced a moderate increase in the power of thoria of giving an emanation, and of exciting radioactivity on surrounding surfaces. We have confirmed and extended his results by the following experiments.

Two similar weights of ordinary thoria were exposed in jars sealed with wax, the one containing sulphuric acid and the other water, for a period of 4 days. The desiccated sample showed 54 per cent. and the sample exposed to water vapour 134 per cent. of the original emanating power. The experiment was repeated and the samples left for a week with much the same result: 70 per cent. and 141 per cent. respectively. It was of interest to see if a more complete desiccation would further reduce the emanating power. Five grams of thoria were sealed up in a tube containing phosphoric oxide, the two substances being separated by a plug of glass wool. Before sealing, the tube was exhausted by a Töpler mercury pump. After 26 days, the end of the tube was connected with a closely packed phosphoric oxide tube, the tip broken off inside the connection, and a slow stream of dried air thus allowed to enter. The other end was connected to the testing cylinder, and arrangements were made to send a stream of air through into the cylinder. When all was ready, this end of the tube was broken inside the connection, and the emanating power

measured. A similar experiment made with an ordinary sample of thoria, using the same arrangement, showed that the desiccated sample possessed 79 per cent. of the emanating power of the ordinary sample tested under the same conditions.

A sample of thoria sprayed with water gave 125 per cent. of its original emanating power. If completely flooded with water, however, the value is much reduced, as would be expected from the reduction of surface.

Another trial was made, in which thoria was flooded with concentrated sulphuric acid. Hardly any emanation was observed so long as the mixture remained undisturbed, but when vigorously shaken it gave nearly one-half of the original emanation.

These experiments show that the presence of water, although producing a marked increase, is not apparently essential for the production of the phenomena. It must be mentioned, however, that thoria only ceases to lose weight after prolonged ignition with the blowpipe, that is, under conditions which nearly destroy its emanating power. This, with analogous points, will be taken up, however, in a separate communication on the more purely chemical side of the question.

The results of some experiments on the effects of other conditions may be shortly tabulated. In each case the sample was exposed to the conditions given for 4 days. The emanating power is that possessed at the end of this period, compared with that of the first sample, which is regarded as 100 per cent. :

1. Kept in sealed test-tube enclosed completely in lead tube .....	100 per cent.
2. Taken from tightly stoppered stock bottle containing the main quantity .....	100 „
3. Sealed up in test-tube and exposed to bright, all-day sun.....	100 „
4. Exposed to the air of the laboratory in open watch glass .....	105 „
5. Kept in a continuous stream of ordinary air .....	88 „

The last experiment was made at a different time from the other four, and therefore is not strictly comparable. The most useful result attained is that thoria does not change in emanating power when kept in closed vessels under different conditions, but when exposed to the air the emanating power varies within comparatively narrow limits.

*Thorium Hydroxide.*—The effect of time on the emanating power of the freshly prepared hydroxide already mentioned is one of the most striking observations in this connection. The following addi-

tional experiments have been made on this point. A quantity of hydroxide was prepared, and separate portions subjected to different drying temperatures and subsequent conditions, as follows :

	Emanating power.
1. Dried at 110° and exposed some hours to the air .....	264 per cent.
2. Dried as before at 110° and kept in desiccator until tested .....	226 „
3. Dried at 200° and kept in desiccator.....	220 „
4. Dried at 250° and kept in desiccator.....	219 „

From this, it appears that the additional loss of water caused by exposure to increasing temperatures is without effect on the emanating power.

A similar experiment to that described for thorium oxide was performed with the hydroxide. Two quantities were exposed in closed bottles to the action of moist air and of air dried with sulphuric acid respectively, and showed, after 4 days, emanating powers of 394 per cent. and 307 per cent. After having been exposed to the air for 24 hours, these samples showed 350 per cent. and 324 per cent. respectively.

The next experiment was designed to include the effect of carbon dioxide, which the hydroxide absorbs from the air to the extent of 2 per cent. of its weight. A quantity of hydroxide was tested immediately after preparation, and possessed 140 per cent. emanating power. A sample was sealed up in a test-tube, while another similar sample was tested in the following manner. It was exposed to a current of moist carbon dioxide for an hour, and then possessed an emanating power of 156 per cent. It was then left exposed to the air of the laboratory and tested at intervals :

After 2 days .....	Emanating power	263 per cent.
„ 6 „ .....	„	325 „
„ 10 „ .....	„	300 „
„ 11 „ .....	„	341 „
„ 16 „ .....	„	362 „

On the last day, the sealed up specimen was opened and examined, and was found to possess an emanating power of 298 per cent. These experiments show that if the air is fundamental in producing the increase of emanating power with time, a very limited quantity of it is effective. For the present, it is perhaps better to consider it as an effect of time simply, hastened no doubt by the presence of water vapour.



*On the Chemical Nature of the Emanation.*

The following work has reference to the emanation itself and not to the material producing it, and was designed to see whether the emanation possesses chemical properties which would identify it with any known kind of matter. It had been noticed at the time of its discovery that it passed unchanged through concentrated sulphuric acid. The same holds true of every reagent that has been investigated.

The effect of temperature was first tried. The air containing the emanation, obtained in the usual way by passage over thoria, was led through the platinum tube heated electrically to the highest attainable temperature, and also through the tube cooled by solid carbon dioxide and ether. The tube was then filled with platinum black, and the emanation passed through in the cold, and with gradually increasing temperatures, until the limit was reached. The effect of the intense heat was to convert the platinum black completely into platinum sponge. In another experiment, the emanation was passed through a layer of red hot lead chromate in a glass tube. The current of air was replaced by a current of hydrogen and the emanation sent through red hot magnesium powder, and red hot palladium black, and, by using a current of carbon dioxide, through red hot zinc dust. In every case, the emanation passed without sensible change in the amount. If anything, a slight increase occurred, owing to the time taken for the gas current to pass through the tubes when hot being slightly less than when cold, the decay *en route* being consequently less. It will be noticed that the only known gases capable of passing in unchanged amount through all the reagents employed are the recently discovered gases of the argon family.

But another interpretation may be put upon the results. If the emanation were the manifestation of excited radioactivity on the surrounding atmosphere, then since from the nature of the experiments it was necessary to employ in each case, as the atmosphere, a gas not acted on by the reagent employed, the result obtained might be explained. Red hot magnesium would not retain an emanation consisting of radioactive hydrogen, or red hot zinc dust an emanation consisting of radioactive carbon dioxide. The correctness of this explanation was tested in the following way. Carbon dioxide was passed over thoria, then through a T-tube, where a current of air met and mixed with it, both passing on to the testing cylinder. But between this and the T-tube, a large soda-lime tube was introduced, and the current of gas thus freed from its admixed carbon dioxide before being tested in the cylinder for emanation. The amount of emanation found was quite unchanged, whether carbon dioxide was

sent over thoria in the manner described, or whether an equally rapid current of air was substituted for it, keeping the other arrangements as before. The theory that the emanation may consist of the surrounding medium rendered radioactive is thus excluded, and the interpretation of the experiments must be that the emanation is a chemically inert gas analogous in nature to the members of the argon family.

It is perhaps early to discuss these results from a theoretical point of view, although it appears certain that an explanation of the nature of the emanation must precede, as a necessary step, any hypothesis put forward to account for emanating power. The explanation already advanced and disproved being left out of the question, two other views of the origin and nature of the emanation are still possible. It may be that one of the inert constituents of the atmosphere is rendered radioactive in the presence of thoria and so constitutes the emanation. The actual amount being probably extremely small, and air being a constant impurity in all gases as ordinarily prepared, it is of course no argument against this view that emanating power is independent of the gaseous medium surrounding the emanating material. An experiment is in progress, however, to ascertain whether emanating power persists in a current of gas as free from air as present methods of preparation allow. The other alternative is to look upon the emanation as consisting of a gas emitted by the thorium compound. It is not necessary that such should contain thorium, it might conceivably be an inert gas continuously emitted in the radioactive state.

In the present state of knowledge, it would be premature to attempt to choose between these two alternatives. But in any decision of this point, the work already given on the regeneration of the emanating power of thoria de-emanated by ignition, the continuous loss of emanating power by successive ignition at increasing temperatures, and the increase in the chemical activity of thorium hydroxide with time, must be taken into consideration.

#### *Concentration of the Radioactive Material.*

Since the preceding account was written, developments have been made in the subject which completely alter the aspect of the whole question of emanating power and radioactivity. The first has reference to thorium nitrate, which in the solid state hardly possesses any emanating power. In a careful determination, using 20 grams of the finely powdered commercial salt, this worked out to be only 1.8 per cent. of the emanating power of thoria. Dissolved in water, however, and tested for emanation by bubbling a current of air through it, it gives about three times as much emanation as thorium

oxide. That is, solution in water increases the emanating power of thorium nitrate nearly 200 times. The emanating power, as in the case of solids, is proportional to the weight of substance present, and within the limits tried is not much affected by dilution, for a solution of 10 grams made up to 25 c.c. in volume possessed a similar value when diluted four times.

Solutions of thorium chloride also give a large amount of emanation.

In these experiments, the cylinder *C* (Fig. 1) is replaced by a Drechsel bottle. A drying tube of calcium chloride is inserted between it and the testing cylinder to prevent the moisture destroying the insulation of the latter. In this connection, the method of testing the insulation by varying the voltage is invaluable. The air current under these circumstances cannot of course be kept so constant as when working with solid substances, and the results are not strictly comparable in consequence, but the arrangement works well enough for a first approximation.

Simultaneously with this observation of the latent emanating power of thorium nitrate, it was noticed that preparations of thorium carbonate varied enormously in emanating power according to their method of preparation. A sample prepared from the nitrate by complete precipitation with sodium carbonate showed an emanating power of 370 per cent. of that of the ordinary oxide, and this value remained fairly constant with time. In another experiment, the precipitated carbonate was partially redissolved in nitric acid, and the redissolved fraction completely reprecipitated with ammonia as hydroxide. The result was remarkable: the carbonate had an emanating power of only 6 per cent., the hydroxide one of 1225 per cent. of that of the ordinary oxide. On repeating the experiments, both fractions proved almost equally inactive, the carbonate showing 14 per cent. and the hydroxide 19 per cent. of the emanating power of thoria. An even greater difference between these two similar experiments was observed in the effects of time on the different preparations. In the first, the carbonate did not alter in value in 7 days, whilst the hydroxide steadily decreased:

	Hydroxide.	Carbonate.
Original.....	1225 per cent.	6.2 per cent.
After 1 day.....	1094    ,,	8.4    ,,
After 4 days .....	696    ,,	4.8    ,,
After 7 days .....	614    ,,	4.7    ,,
After 14 days .....	473    ,,	—

In the second experiment, the emanating power of both the carbonate and hydroxide had increased many fold when tested 11 days later, and

the former now possessed 109 per cent., the latter, 273 per cent. (originally 14 per cent. and 19 per cent. respectively).

The straight line radioactivity of the carbonate from the first experiment which possessed such a low emanating power is of interest. It proved to be similar to that of a specimen of hydroxide of normal emanating power, which it resembled in density and state of division. After having been kept 7 days without showing any sign of recovering its emanating power, it was redissolved in nitric acid, and reprecipitated with ammonia as hydroxide. The latter now possessed, when first made, an emanating power of 65 per cent., and after 24 hours 145 per cent., from which value it did not much alter.

These results throw a new light on the question of emanating power. In the first experiment, which we have so far not succeeded in repeating, by an accident in the conditions apparently, two fractions were separated from thorium which varied in their emanating power in the ratio of 200 to 1. The active fraction diminished to nearly a third of its original value in 14 days spontaneously, whilst the activity of the inactive fraction was, to a large extent, regenerated by solution and reprecipitation, in an exactly analogous manner to the behaviour of thoria de-emanated by ignition. Attempts to repeat this result have so far led to the production of two more or less completely de-emanated fractions, which, however, spontaneously increase in activity with time, as in the second experiment, and this seems to be generally the case, whether incomplete precipitation is effected as in the experiment given by re-solution of the carbonate in acid, or by using a deficiency of sodium carbonate in the first instance.

The production of preparations of such low emanating power led naturally to an examination being made of the filtrates and washings for radioactivity. It was found that these possess when concentrated both emanating power and radioactivity in considerable amounts, although from the nature of their production they should be chemically free from thorium. The behaviour is quite general, a dilute solution of thorium nitrate, after the thorium has been precipitated as hydroxide with ammonia, shows when concentrated an emanating power of from one-third to two-thirds that of the original nitrate in solution. It does not matter whether the thorium is precipitated with ammonia directly, or after preliminary partial precipitation as carbonate—either by adding insufficient sodium carbonate in the first place, or by precipitating completely and dissolving part of the precipitate in nitric acid—the thorium-free filtrate invariably possessed emanating power, and when evaporated to dryness exhibited straight line radioactivity also in amounts very much greater than possessed by the same weight of thoria.

The result of a careful chemical investigation of the active filtrates

produced under the various conditions described was to show that these contained no thorium, or at most only a minute trace, but another substance in very appreciable quantities which can be precipitated with sodium phosphate, and which, so prepared, is a white substance possessing both emanating power and radioactivity, often many hundred-fold greater than thoria. It has not yet been obtained in sufficiently large quantities for an exhaustive chemical investigation, and it is impossible at present to say what it may prove to be.

We may at once state, however, that we do not incline to the view that it is ThX, either in the sense of the radioactive or emanating constituent of thorium. The evidence of a long series of experiments in two directions, of which the final steps can only find place here, is quite definite on this point, and in our opinion admits of only one conclusion. There seems little doubt of the actual existence of a constituent ThX to which the properties of radioactivity and emanating power of thorium must be ascribed, but in all probability it is present in altogether minute amount, and must therefore be possessed of these qualities to a correspondingly intense degree.

But before the reasons for this view are put forward, it is necessary to discuss more nearly the meaning of the experiments already given on the emanating power. It has been shown that this is a most uncertain quantity, similar experiments often giving preparations of very varying value, as is clearly shown in the results given, as well as in many others in the same direction. The most pregnant fact is that although, as has been shown, precipitation with ammonia invariably leaves behind considerable emanating material in the filtrate which is lost, this seems to exert little influence on the emanating power of the precipitates. These, prepared under different conditions, often by a different number of precipitations, in which therefore varying amounts of the emanating material are lost, show a surprising uniformity in this property, especially after they have attained their maximum power by keeping. It is only necessary to quote the experiment on the almost completely de-emanated carbonate, which gained in emanating power thirty times by conversion into the hydroxide, although during the process much emanating material must have been lost, to show that the value of the emanating power alone furnishes no criterion of the amount of emanating material present.

It may safely be said that three things must be carefully distinguished between in considering the nature of the property possessed by thoria of giving out a radioactive emanation. First, the nature of the emanation itself, secondly, the nature of the emanating power, and thirdly, the nature of the emanating material. The first, the emanation itself, we have shown to possess the negative properties of a chemically inert gas, whose radioactivity is unaffected by any con-

ditions, apparently, except lapse of time. With regard to the second, the emanating power or *rate* at which the emanation is produced per unit weight of substance, it is certain that this does not depend only, or even mainly, on the quantity of emanating material present. The regeneration of the emanating power of thoria de-emanated by ignition, the enormous variation with time in the emanating power of the hydroxide and carbonate under certain conditions, and the comparatively constant maximum which these substances ultimately attain, although prepared under conditions where different amounts of the emanating material are lost, make this point perfectly clear. These considerations, taken in conjunction with the effect of temperature, moisture, &c., on emanating power, and the nature of the emanation itself, make the property appear rather as the result of a dynamical change, possibly in the nature of a chemical reaction where the active mass of emanating material is a constant, than as the property of a peculiar kind of matter in the static state, additive with regard to mass.

It is, however, neither the emanation itself nor the emanating power with which we are concerned in these experiments, but the third conception, the emanating material, that is, the substance, whether thorium or not which is responsible for the activity. It has been shown that it is difficult to follow, by means of the value of the emanating power, the progress of the removal of the active material. When this was realised, attention was directed to the straight line radioactivity, which is generally unaffected by these changes of conditions and previous history which produce such profound alteration in the former property. The two phenomena are undoubtedly connected. The intensely radioactive preparations obtained from thorium in different ways always show correspondingly great emanating power when the conditions are favourable for the manifestation of the latter. Solution appears to be the most generally favourable condition. The experiments we had been engaged in were therefore repeated in a form which would allow a close study of the total radioactivity, in the hope that this value would prove a more suitable indication of the amount of active material present than the emanating power alone.

Seventy grams of thorium nitrate were dissolved in four litres of boiling water, and precipitated with ammonia added cautiously in very dilute solution in excess. The filtrates and washings were evaporated to about 60 c.c. and then possessed as much emanating power as 146 grams of thoria. On evaporating the solution to dryness and removing the ammonium salts by ignition the residue weighed 0.0583 gram. The emanating power of this residue in solution was thus about 2500 times that of ordinary thoria. In the solid state, however, the value fell to one-fiftieth. But its total radiation was equivalent to at least 23.6 grams of thoria, that is, was about 400 times as

great. It was dissolved in hydrochloric acid, and ammonia added in excess, when a precipitate weighing 0.0015 gram was thrown down. This contained all the thorium present besides iron in appreciable quantity which had been introduced during the evaporation. It equalled in radioactivity 2.73 grams of thoria, the ratio in this case being thus no less than 1800 times. Sodium phosphate precipitated 0.0225 gram of white substance the activity of which was equivalent to 4.4 grams of thoria, that is, 200 times. The sodium salts freed from ammonium still possessed a radioactivity equivalent to 3.6 grams of thorium oxide. In other experiments, however, these had been obtained quite free from activity, and this result is due to the solubility of the phosphate in water, so that some was dissolved during the washing (which the subsequent determination of the weight rendered necessary) and appeared in the filtrate.

The radioactive residue obtained in the first place from the filtrate by evaporation and ignition, before it was redissolved, had, however, been tested to determine the penetrative power of the radiations emitted. If the rays from various radioactive substances are made to pass through successive layers of aluminium foil, each additional layer of foil cuts down the radiation to a fraction of its former value, and a curve can be plotted with the thickness of metal penetrated as abscissæ, and the intensity of the rays after penetration as ordinates, expressing at a glance the penetrative power of the rays being examined (compare Rutherford, *Phil. Mag.*, 1899, [v], 47, 122). The curves so obtained are quite different for different radioactive substances. The radiations from uranium, radium, thorium, each give distinct and characteristic curves, whilst that of the last named again is quite different from that given by the excited radioactivity produced by the thorium emanation. The examination in this way of the penetrative power of the rays from the radioactive residue showed that the radiations emitted were in every respect identical with the ordinary thorium radiation. In another experiment, the nature of the emanation from a similar intensely active thorium-free residue was submitted to examination. The rate of decay was quite indistinguishable from that of the ordinary thorium emanation. That is, substances chemically free from thorium have been prepared possessing thorium radioactivity in an intense degree.

The main quantity of thorium hydroxide in the last experiment was redissolved in nitric acid, and the previous round of operations repeated twice, the filtrates from each operation being mixed and then examined exactly as in the former case. The emanating power of the concentrated solution was only equal to that of 8 grams of thoria in this instance, and the radioactivity of the residue to that of 3 grams.

From this only a small quantity of the phosphate precipitate was

obtained (0.001 gram) the radioactivity of which was equal to that of 0.3 gram of thoria (ratio 200 : 1).

The *emanating power* of the main quantity of the hydroxide when first so prepared was 73 per cent. that of thoria, that is, about one-half of its usual value. The hydroxide was converted into oxide by ignition, and its *radioactivity* compared with that of the oxide from the original nitrate prepared in the same way. It was found to be only about one-third as active, the exact ratio being 0.36 : 1.

Only one conclusion seems possible from this series of experiments. There is no longer any room for doubt that a part of the radioactive constituent ThX has been separated from thorium, and obtained in a very concentrated form, in one instance 1800 times more powerful in its actions. This result, taken into account with the reduction of the radioactivity and emanating power of the main quantity of thorium compound, and the identity of the radiations of the active thorium-free preparations with those of the ordinary thorium radiation, warrant the conclusion that ThX is a distinct substance, differing from thorium in its chemical properties and so capable of separation therefrom. The manner in which it makes its appearance, associated with each precipitate formed in its concentrated solution, resembles the behaviour of Crookes' UrX, which he found was dragged down by precipitates when no question of insolubility is involved, and suggests the view that it is really present in minute quantity. Even in the case of the most active preparations, these probably are composed of some ThX associated with accidental admixtures probably large in proportion.

These results receive confirmation from observations made in a different method of separating ThX. The experiment was tried of washing thoria with water repeatedly, and seeing if the radioactivity was thereby affected. In this way, it was found that the filtered washings, on concentration, deposited small amounts of material, with an activity often of the order of a thousand times greater than that of the original sample. In one experiment, 290 grams of thoria were shaken for a long time with nine quantities, each of 2 litres, of distilled water. The first washing, containing most of the sulphate already referred to, was rejected, the rest concentrated to different stages, and filtered at each stage. One of the residues so obtained weighed 6.4 mg. and was equivalent in radioactivity to 11.3 grams of the original thoria, and was therefore no less than 1800 times more radioactive. It was examined chemically, and gave, after conversion into sulphate, the characteristic reaction of thorium sulphate, being precipitated from its solution in cold water by warming. *No other substance than thorium could be detected by chemical analysis*, although of course the quantity was too small for a minute examination. But the absence of the substance precipitable as phosphate, noticed in the other experi-



ments, confirms the opinion that this is an accidental admixture without influence on the qualities of radioactivity and emanating power. The penetrative power of the radiation from this substance again established its identity with the ordinary thorium radiation. In another experiment, a small quantity of thoria was shaken many times with large quantities of water. In this case, the radioactivity of the residue was examined and found to be about 20 per cent. less radioactive than the original sample.

There remains only one step to prove beyond doubt that the radioactivity and emanating power of thorium are not specific properties of the thorium molecule—the preparation of thoria free from these properties—and on this problem we are now engaged. To sum up briefly what has already been accomplished, two different methods have effected a concentration of the activity many hundred-fold in one fraction, and a corresponding diminution of activity in the remainder, but in each case the character of the radiation is not thereby affected. In one method, the active fraction appears to consist only of thorium, so far as examination has been possible, whilst in the other case radioactivity and emanating power appear to be manifested indiscriminately in all the products, without reference to their chemical nature. The simplest explanation of this behaviour, on the present view, is that so far the active constituent of thorium has only been obtained in relatively minute quantity, and therefore does not answer to any definite analytical reactions.

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#### XXXIV.—*Solubilities of the Calcium Salts of the Acids of the Acetic Series.*

By JOHN S. LUMSDEN, D.Sc., Ph.D.

It is well known that many calcium salts are more soluble in water at low than at high temperatures. This is not in accordance with the usual experience that the solubility of a solid increases with rise of temperature, yet the matter has never been submitted to careful investigation.

For the purpose of obtaining more information on the subject, it seemed best to select a series of acids, to prepare the calcium salts in a crystalline state, and to determine the solubility of each salt for a range of temperature between 0° and 100°.

The acetic series of organic acids was chosen and the calcium salts

of the first nine normal acids and of *isobutyric* and *isovaleric* acids have been prepared and examined.

In order to obtain accurate results, the estimation of the solubility of a substance must be done with very great care. The difficulties to be overcome are: the maintenance of a constant temperature for many hours, the production of complete saturation and the removal of the solution from contact with the solid to another vessel without change or loss.

The apparatus used to obtain a constant temperature is shown in Fig. 1 (p. 352). The thermostat is an enamelled iron vessel supported on bricks and heated from below by a luminous gas jet and a ring air burner.

The temperature regulator consists of two bottles filled with water or calcium chloride solution, one of which is shown at *A* connected with an ordinary mercury gas cut-off, *B*. By means of Y glass connections, the gas flame, the ring burner, and the fan jet, *C*, are supplied with gas from the tap, *D*.

For high temperatures, the luminous gas flame connected with the regulator does not produce sufficient heat and the ring burner is then used, being set to keep up a constant temperature less than that required and the gas flame then raises the temperature to the exact point and regulates it.

The water level is kept constant by the syphon, *E*. When the water sinks below the bell-mouthed tube, air enters and water flows from the bottle until the level rises and shuts off the supply of air.

The stirrer, *F*, is mounted on a steel point running in a hole in a glass stopper and moved by a wheel made of Japanese fans. At low temperatures, the fan jet is required, but at high temperatures the heated air from the apparatus causes a sufficiently rapid rotation.

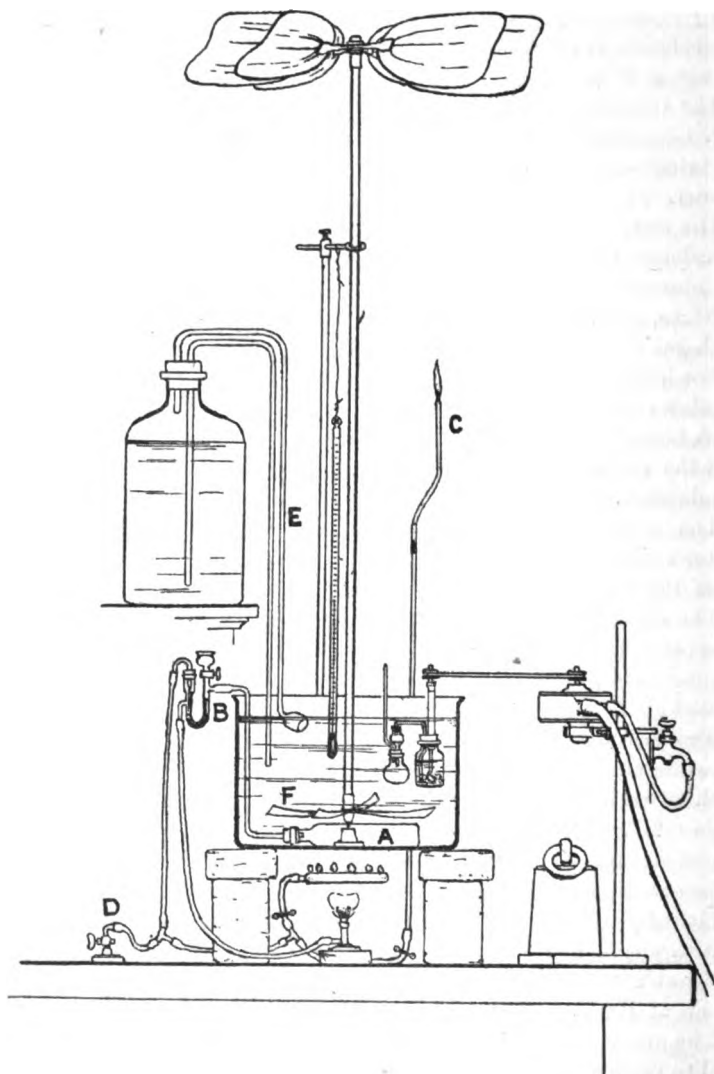
The thermometer used reads to tenths of a degree, and for temperatures between 20° and 90° the water in the thermostat can be kept without variation of more than one-fifth of a degree for many hours. Below 20°, constant temperatures were obtained by running a continual stream of water from the laboratory tap into the vessel. On different days the temperature varied, but on the same day it was sufficiently constant for six hours. Temperatures down to 6° were got in this way. For estimations at the freezing point a mixture of ice and water was used and boiling water was employed for the determinations at 100°.

The apparatus used to obtain complete saturation of the solution and to remove the saturated liquid is shown in Fig. 2 (p. 353), and on a small scale in Fig. 1 (p. 352).

The object in view when this apparatus was devised was to carry out all the operations under the surface of the water in the thermostat and therefore exactly at the temperature of estimation.

The saturating vessel, *G*, is a bottle or small flask into which excess of finely powdered solid is placed along with the solvent. A glass stirrer running in a glass collar and passing down the outer tube, *H*, is driven by

FIG. 1.



a water motor as shown in Fig. 1. *K* is the flask or bottle into which the saturated liquid is to be filtered. The bulb, *L*, is the filter and contains a very small filter paper filled with cotton wool, which keeps the

paper in position and also acts as a filter plug. Connection is made with the saturating vessel by the tube *M*, and the tube *N*, rising above the water level, is the suction tube. The filter flask is not attached to the saturating vessel until a short time before filtering, since at high temperatures water is liable to distil through the tube *M*. The end of that tube is therefore plugged while saturation is taking place.

All the stoppers are of rubber except that which bears the neck of the stirrer, and this has a notch to prevent increase of pressure in the bottle.

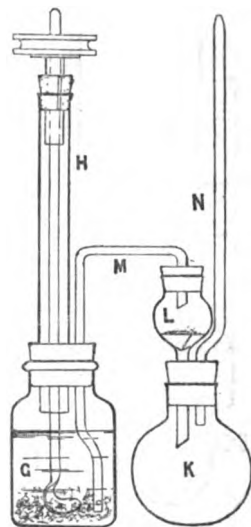
After saturation has been attained, which at low temperatures is only after many hours but at high temperatures is complete in an hour, the filter flask is attached, ten minutes are allowed for heating to the temperature of the bath, then suction is applied by the mouth to *N*, and the liquid passes over and filters quite clear into the flask. As much as possible of the liquid is filtered, to reduce any error due to absorption by the filter or moisture in the connecting tube.

After filtration, the flask is quickly detached, corked and immediately cooled to the temperature of the laboratory by running water on the outside. This quick cooling prevents evaporation taking place and consequent concentration of the solution.

It is necessary to know the exact composition of the solid of which a saturated solution is being made, as the solid may undergo change. An anhydrous salt, when placed in water, may become a crystalline hydrate and a salt containing water of crystallisation may lose water in contact with a hot solution. As a salt and its hydrates are essentially different substances, they have different solubilities, and analysis is necessary to determine the substance being dealt with.

The apparatus used for separating the solid at any temperature from the saturated solution is seen in Fig. 3 (p. 354). The tube *O*, used as the saturating vessel, has a rubber stopper fitted to the lower end, and through a hole in this passes a glass tube which makes connection with the filter bottle. A rubber connection with a screw clip keeps the tube closed until filtration is to take place. On the rubber stopper rest two perforated porcelain plates with a filter paper between. The solid is placed in the tube, the solvent added, and saturation attained at the desired temperature. The clip is then opened, the tube

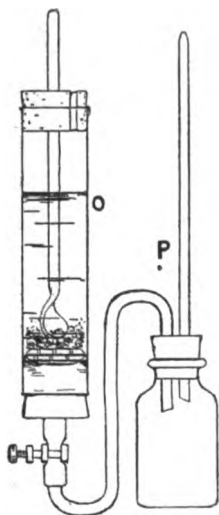
FIG. 2.



*P* attached to a filter pump, and while suction is going on the solid is rammed down tightly to express as much solvent as possible. The apparatus is then quickly removed from the thermostat and the solid placed on a warmed porous plate. Drying is speedily effected, and after an hour in a desiccator the solid is analysed before any change can take place. With all precautions, it is difficult in many cases to get exact quantitative results: either the solid is insufficiently dried or water of crystallisation is lost, but there is no difficulty in getting results which show decidedly whether the solid is one or other of two hydrates.

The saturated solutions obtained in these determinations and the solids containing calcium had to be analysed, and this is a tedious and difficult process unless the following method is adopted.

FIG. 3.



It was found most exact to convert the calcium compounds always into calcium sulphate. From 5 to 10 grams of the solution were placed in a platinum crucible and weighed, then somewhat less than the quantity of concentrated sulphuric acid required to complete the change to calcium sulphate was added. When the crucible was heated on a water-bath, the organic acid rapidly evaporated, and a hard residue was obtained in an hour. This was carefully ignited, and the dried mass, consisting of oxide, sulphide, and sulphate of calcium, was treated again with concentrated acid and heated until fumes ceased to be evolved and the residue was pure white.

The calcium salts employed in the following determinations were prepared from the pure acids obtained from Kahlbaum and from precipitated calcium carbonate. A quantity of the acid was largely diluted with water, enough water being used in the case of the higher acids, which are only slightly soluble, to form a complete solution, and this was then poured on excess of calcium carbonate contained in a large flask. After the first action ceased, heat was applied for some time, and the liquid was then filtered.

This filtered solution was always slightly acid, and it was found that when organic acids become very dilute they cease to act on calcium carbonate. Since all the acids are volatile, the acidity disappeared during evaporation of the liquid. The solid obtained by evaporation over a water-bath was dissolved in water, and crystals obtained by placing the vessel in a warm place, and occasionally removing and drying those which separated.

Most of these calcium salts are soluble in hot dilute alcohol, and it was found easiest to obtain good crystals of the higher members from such a solution.

*Solubility of Calcium Formate,  $(\text{HCO}_2)_2\text{Ca}$ . Curve No. 1.*

Calcium formate crystallises from solution in water or dilute alcohol in anhydrous, hard, glass-like, rhombic crystals. Attempts to obtain a hydrated salt by spontaneous evaporation of a solution in water at a low temperature were unsuccessful:

0.9616 crystals gave 1.0021  $\text{CaSO}_4$ .  $\text{Ca} = 30.7$ .

$(\text{CHO}_2)_2\text{Ca}$  requires  $\text{Ca} = 31.2$  per cent.

The solubility curve of calcium formate between  $0^\circ$  and  $100^\circ$  is a straight, upwardly inclined line, representing a steadily increasing solubility with rise of temperature.

The weights of solid dissolved by 100 parts by weight of water are as follows:

t.	Parts.	t.	Parts.	t.	Parts.
$0^\circ$	16.15	$40^\circ$	17.05	$80^\circ$	17.95
10	16.37	50	17.27	90	18.17
20	16.60	60	17.50	100	18.40
30	16.82	70	17.72		

Formula for this range of temperature,  $16.15 + 0.0225t^\circ$ .

*Solubility of Calcium Acetate,  $(\text{CH}_3\cdot\text{CO}_2)_2\text{Ca}, 2\text{H}_2\text{O}$  and  $(\text{CH}_3\cdot\text{CO}_2)_2\text{Ca}, \text{H}_2\text{O}$ . Curve No. 2.*

From a cold solution, calcium acetate crystallises in long, silky, transparent needles which contain 2 mols. of water of crystallisation. These effloresce readily, and the ordinary white solid contains only 1 mol. of water:

1.066 gave 0.8230  $\text{CaSO}_4$ .  $\text{Ca} = 22.71$ .

$(\text{C}_2\text{H}_3\text{O}_2)_2\text{Ca}, \text{H}_2\text{O}$  requires  $\text{Ca} = 22.73$  per cent.

In solution, the change from the salt with  $2\text{H}_2\text{O}$  to that with  $1\text{H}_2\text{O}$  takes place at  $84^\circ$ .

The solubility at  $0^\circ$  is 37.40 parts in 100 parts of water; it then diminishes until about  $60^\circ$ , when the solution contains only 32.70 parts, then rises until the transition point is reached at  $84^\circ$ , when 33.80 parts are dissolved. From  $84^\circ$ , the solubility of the new salt diminishes rapidly to  $100^\circ$ , when the solution contains 29.65 parts.

The weights of solid, calculated as anhydrous salt, dissolved by 100 parts of water, are as follows:

t.	Parts.	t.	Parts.	t.	Parts.
(2H <sub>2</sub> O) 0°	37·40	(2H <sub>2</sub> O) 35°	33·50	(2H <sub>2</sub> O) 70°	32·98
5	36·65	40	33·22	75	33·22
10	35·98	45	33·00	80	33·50
15	35·32	50	32·82	T 84	33·80
20	34·73	55	32·70	(H <sub>2</sub> O) 85	32·85
25	34·20	60	32·70	90	31·05
30	33·82	65	32·78	95	30·20
				100	29·65

*Solubility of Calcium Propionate, (CH<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>)<sub>2</sub>Ca, H<sub>2</sub>O.*  
Curve No. 3.

The crystals of calcium propionate are thin, glistening plates containing 1 mol. of water of crystallisation, which is only given off above 100°.

The solubility curve is markedly convex to the temperature axis. At 0°, as much as 42·80 parts of the salt dissolve in 100 parts of water, but the solubility quickly diminishes until, at about 55°, only 38·20 parts are in solution. Above this temperature, the solubility increases and at 100° 48·44 parts are dissolved.

To make sure that the solid in contact with the solution was the same on the descending and ascending parts of the curve, it was filtered off at various temperatures and analysed. The results showed that at all temperatures the solid contained 1 mol. of water :

At 12°, 0·1739 gave 0·1159 CaSO<sub>4</sub>. Ca = 19·61.

„ 90°, 0·3895 „ 0·2591 CaSO<sub>4</sub>. Ca = 19·57

(Ca<sub>3</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>Ca, H<sub>2</sub>O requires Ca = 19·61 per cent.

The weights of solid dissolved by 100 parts of water are as follows :

t.	Parts.	t.	Parts.	t.	Parts.
0°	42·80	35°	38·75	70°	38·75
5	41·70	40	38·45	75	39·20
10	40·95	45	38·35	80	39·85
15	40·35	50	38·25	85	40·80
20	39·85	55	38·20	90	42·15
25	39·40	60	38·25	95	44·25
30	39·05	65	38·40	100	48·44

*Solubility of Calcium Butyrate, [CH<sub>3</sub>·(CH<sub>2</sub>)<sub>2</sub>·CO<sub>2</sub>]<sub>2</sub>Ca, H<sub>2</sub>O.*  
Curve No. 4.

Calcium butyrate crystallises by spontaneous evaporation in long, ribbon-like leaves containing 1 mol. of water, and this is the compo-

sition of the solid in contact with the solution at all temperatures below 100° :

0.4940 gave 0.2898  $\text{CaSO}_4$ .  $\text{Ca} = 17.26$ .

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, \text{H}_2\text{O}$  requires  $\text{Ca} = 17.24$  per cent.

The solubility of this substance has been determined by Hecht (*Annalen*, 1882, 213, 65) and by Chancel and Parmentier (*Compt. rend.*, 1887, 104, 474). Their results are slightly lower than those given below.

The weight, calculated as anhydrous salt, in 100 parts of water is as follows :

t.	Parts.	t.	Parts.	t.	Parts.
0°	20.31	35°	16.70	70°	14.92
5	19.75	40	16.40	75	14.90
10	19.15	45	16.00	80	14.95
15	18.65	50	15.70	85	15.10
20	18.20	55	15.40	90	15.25
25	17.75	60	15.15	95	15.50
30	17.25	65	15.00	100	15.85

*Solubility of Calcium Valerate,  $[\text{CH}_3 \cdot (\text{CH}_2)_3 \cdot \text{CO}_2]_2\text{Ca}, \text{H}_2\text{O}$ .*

*Curve No. 5.*

Calcium valerate is obtained from solution in hot water as a micro-crystalline powder, but if a cold solution is allowed to evaporate, fine, interwoven crystals are obtained, and from dilute alcohol long, ribbon-like plates readily separate out.

One mol. of water is always present below 100° :

0.4219 crystals gave 0.2210  $\text{CaSO}_4$ .  $\text{Ca} = 15.41$ .

$(\text{C}_5\text{H}_9\text{O}_2)_2\text{Ca}, \text{H}_2\text{O}$  requires  $\text{Ca} = 15.38$  per cent.

The solubility for each 10° is as follows :

t.	Parts.	t.	Parts.	t.	Parts.
0°	9.82	50°	7.85	70°	7.80
10	9.25	55	7.76	80	7.95
20	8.80	57	7.75	90	8.20
30	8.40	60	7.78	100	8.78
40	8.05				

The point of lowest solubility is 57°, when only 7.75 parts of solid are in solution.



*Solubility of Calcium Caproate (Hexoate),*  $[\text{CH}_3 \cdot (\text{CH}_2)_4 \cdot \text{CO}_2]_2\text{Ca}, \text{H}_2\text{O}.$   
*Curve No. 6.*

This salt separates from water in small, leafy crystals, but long, thin plates are obtained from hot dilute alcohol. One mol. of water is present up to  $100^\circ$ :

0.4580 gave 0.2162  $\text{CaSO}_4$ .  $\text{Ca} = 13.89$ .

$(\text{C}_6\text{H}_{11}\text{O}_2)_2\text{Ca}, \text{H}_2\text{O}$  requires  $\text{Ca} = 13.89$  per cent.

The solubility curve, although very flat, distinctly shows a descending and an ascending part, the point of lowest solubility being about  $55^\circ$ .

The solubility for each  $10^\circ$  is as follows:

t.	Parts.	t.	Parts.	t.	Parts.
$0^\circ$	2.23	$40^\circ$	2.15	$80^\circ$	2.30
10	2.20	50	2.10	90	2.45
20	2.18	60	2.15	100	2.57
30	2.17	70	2.20		

*Solubility of Calcium Enanthate (Heptoate),*  $[\text{CH}_3 \cdot (\text{CH}_2)_5 \cdot \text{CO}_2]_2\text{Ca}, \text{H}_2\text{O}.$   
*Curve No. 7.*

The crystals from dilute alcohol are long, monoclinic prisms forming a fibrous, silky mass. They contain 1 mol. of water:

0.098 gave 0.0424  $\text{CaSO}_4$ .  $\text{Ca} = 13.52$ .

$(\text{C}_7\text{H}_{13}\text{O}_2)_2\text{Ca}, \text{H}_2\text{O}$  requires  $\text{Ca} = 12.88$  per cent.

The solubility is as follows:

t.	Part.	t.	Part.	t.	Part.
$0^\circ$	0.95	$40^\circ$	0.82	$80^\circ$	0.98
10	0.90	50	0.80	90	1.10
20	0.86	60	0.82	100	1.26
30	0.84	70	0.90		

*Solubility of Calcium Caproate (Octoate),*  $[\text{CH}_3 \cdot (\text{CH}_2)_6 \cdot \text{CO}_2]_2\text{Ca}, \text{H}_2\text{O}.$   
*Curve No. 8.*

As caproic and pelargonic acids are very slightly soluble in water, the calcium salts were prepared by first making the ammonium salts and then adding calcium chloride solution. The precipitated salts were well washed and crystallised from dilute alcohol.

The crystals of calcium caproate are long, thin rhombic needles containing 1 mol. of water.

0.3420 gave 0.1350  $\text{CaSO}_4$ .  $\text{Ca} = 11.61$ .

$(\text{C}_8\text{H}_{15}\text{O}_2)_2\text{Ca}, \text{H}_2\text{O}$  requires  $\text{Ca} = 11.62$  per cent.

The greatest solubility is at 100°, when 0.5 part dissolves in 100 parts of water; the lowest is about 60°, where 0.24 part is in solution:

t.	Part.	t.	Part.	t.	Part.
0°	0.33	40°	0.28	80°	0.32
10	0.32	50	0.26	90	0.40
20	0.31	60	0.24	100	0.50
30	0.30	70	0.28		

*Solubility of Calcium Pelargonate (Nonoate),*  $[\text{CH}_3 \cdot (\text{CH}_2)_7 \cdot \text{CO}_2]_2\text{Ca}, \text{H}_2\text{O}$ .  
Curve No. 9.

Calcium pelargonate forms long, transparent, leafy crystals which, massed together, resemble white satin in lustre. The crystals are readily obtained from solution in hot dilute alcohol. One mol. of water is present:

0.3208 gave 0.1170  $\text{CaSO}_4$ .  $\text{Ca} = 10.73$ .

$(\text{C}_9\text{H}_{17}\text{O}_2)_2\text{Ca}, \text{H}_2\text{O}$  requires  $\text{Ca} = 10.75$  per cent.

The solubility is now very small:

t.	Part.	t.	Part.	t.	Part.
0°	0.16	40°	0.13	80°	0.15
10	0.15	50	0.13	90	0.18
20	0.14	60	0.12	100	0.26
30	0.14	70	0.12		

*Solubility of Calcium isobutyrate,*  $[(\text{CH}_3)_2\text{CH} \cdot \text{CO}_2]_2\text{Ca}, 5\text{H}_2\text{O}$  and  
 $[(\text{CH}_3)_2\text{CH} \cdot \text{CO}_2]_2\text{Ca}, \text{H}_2\text{O}$ . Curve No. 10.

From solution at low temperatures, calcium isobutyrate crystallises in long, thick, prismatic needles containing 5 mols. of water of crystallisation:

0.5648 gave 0.2516  $\text{CaSO}_4$ .  $\text{Ca} = 13.10$ .

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, 5\text{H}_2\text{O}$  requires  $\text{Ca} = 13.16$  per cent.

The crystals filtered from a saturated solution above 80° contain 1 mol. of water:

0.5062 gave 0.2964  $\text{CaSO}_4$ .  $\text{Ca} = 17.22$ .

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, \text{H}_2\text{O}$  requires  $\text{Ca} = 17.24$  per cent.

The transition point from one salt to the other is at 62.5°, and the solubility is represented by two curves.

The weights of anhydrous salt dissolved by 100 parts by weight of water are:

t.	Parts.	t.	Parts.	t.	Parts.
(5H <sub>2</sub> O) 0°	20·10	(5H <sub>2</sub> O) 35°	24·55	(H <sub>2</sub> O) 65°	28·25
5	20·52	40	25·28	70	27·75
10	21·10	45	26·05	75	27·32
15	21·70	50	26·80	80	27·00
20	22·40	55	27·60	85	26·70
25	23·10	60	28·40	90	26·48
30	23·80	T 62	28·70	95	26·28
				100	26·10

The solubility of calcium *isobutyrate* was determined in 1887 by Chancel and Parmentier (*Compt. rend.*, 1887, 104, 474). At low temperatures, their values approximate to those now found, but although they knew that above 80° the salt contained only 1 mol. of water, yet they show no transition point, but represent the solubility by a simple curve, concave to the temperature axis. Possibly by joining a few distant points, they missed the transition point.

*Solubility of Calcium isoValerate*, [(CH<sub>3</sub>)<sub>2</sub>CH·CH<sub>2</sub>·CO<sub>2</sub>]<sub>2</sub>Ca, 3H<sub>2</sub>O and [(CH<sub>3</sub>)<sub>2</sub>CH·CH<sub>2</sub>·CO<sub>2</sub>]<sub>2</sub>Ca, H<sub>2</sub>O. *Curve No. 11.*

Calcium *isovalerate* crystallises in two forms: in long, thick, well-formed, prismatic needles containing 3 mols. of water, and from a hot solution in thin plates containing 1 mol. of water:

0·2796 gave 0·1289 CaSO<sub>4</sub>. Ca = 13·56.

(C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>)<sub>2</sub>Ca, 3H<sub>2</sub>O requires Ca = 13·52 per cent.

The crystals filtered from a saturated solution above 80° were pressed on a porous plate and placed in a desiccator until they showed signs of efflorescence:

0·8758 gave 0·4626 CaSO<sub>4</sub>. Ca = 15·53.

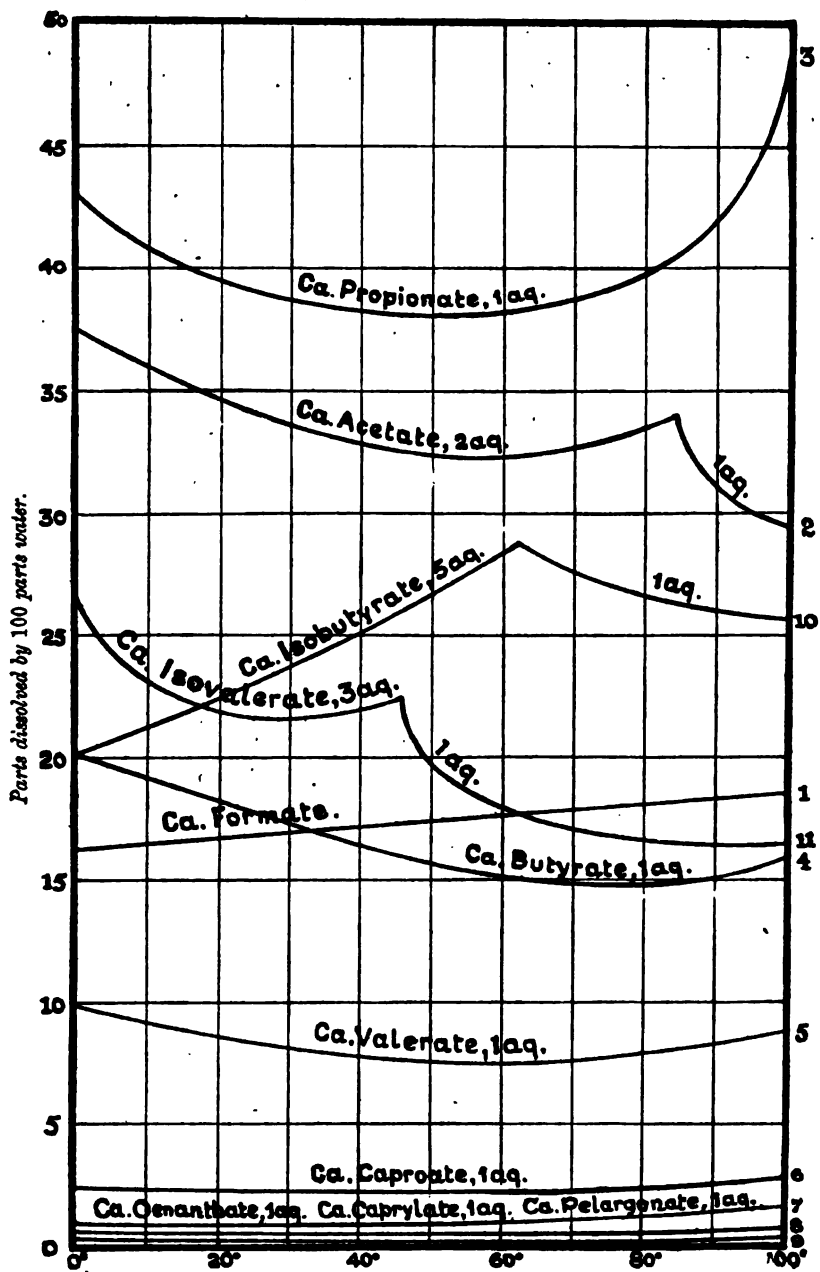
(C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>)<sub>2</sub>Ca, H<sub>2</sub>O requires Ca = 15·38 per cent.

The solubility is shown by two well-marked descending curves, the transition point being at 45·5°.

The weights of anhydrous solid in 100 parts of water at different temperatures are as follows:

t.	Parts.	t.	Parts.	t.	Parts.
3H <sub>2</sub> O 0°	26·05	(3H <sub>2</sub> O) 40°	22·00	(H <sub>2</sub> O) 70°	17·40
5	23·75	45	22·30	75	17·10
10	22·70	T 45·5	22·35	80	16·88
15	22·15	(H <sub>2</sub> O) 50	19·95	85	16·75
20	21·80	55	19·00	90	16·65
25	21·68	60	18·38	95	16·58
30	21·68	65	17·85	100	16·55
35	21·80				

FIG. 4.



Solubility curves of the calcium salts of acids of the acetic series.

The examination of the collected solubility curves (Fig. 4, p. 361) shows the following points :—Calcium formate, the salt of the lowest acid of the series, is peculiar ; it consists of anhydrous crystals, and shows a simple ascending curve of solubility. All the other calcium salts crystallise with water, and all with rise of temperature first diminish in solubility then reach a minimum point, and thereafter the solubility steadily increases.

Of the salts of the normal acids, only calcium acetate changes from one crystalline state to another between  $0^{\circ}$  and  $100^{\circ}$ , while both calcium isobutyrate and calcium isovalerate have double curves. It will also be noticed that, with the exception of calcium formate, all the salts which have been investigated, when in contact with their saturated solutions at  $100^{\circ}$ , consist of crystals which contain 1 mol. of water.

Whilst it is difficult to compare a series of salts with respect to solubility, since one may be more soluble than another at one temperature, but less soluble at a different temperature, and different hydrates are not truly comparable, yet in a general sense it may be said of the calcium salts under consideration that those formed from the normal acids increase in solubility from formate to acetate and propionate, then decrease quickly with the growth in the number of carbon atoms, and that the salts of the *iso*-acids are more soluble than those of the corresponding normal members of the series.

As the solubilities of these calcium salts with rise of temperature diminish, reach a minimum, and then increase, each curve is convex to the temperature axis, and it will be shown in the following paper that this is the normal shape of a solubility curve. Calcium salts will be found to be in no wise anomalous in diminishing in solubility with rise of temperature ; they are simply peculiar in having the descending parts of their curves within the range of temperature between  $0^{\circ}$  and  $100^{\circ}$ , whilst the curves of most other solids are the ascending parts of convex curves, which would show a minimum and descending part if the determination of the solubility could be made at a low enough temperature.

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### XXXV.—*The Equilibrium between a Solid and its Saturated Solution at Various Temperatures.*

By JOHN S. LUMSDEN, D.Sc., Ph.D.

IN the foregoing paper, it was shown that the solubilities of the calcium salts of the acids of the acetic acid series were represented by curves convex to the temperature axis, indicating at first decrease then increase of solubility with rise of temperature.

As these salts, while undergoing no alteration in composition, yet change in solubility in such a way that at widely different temperatures the action of the solvent produces solutions of equal concentration, the factors which condition the equilibrium between the solid and the saturated solution must undergo great variation with change of temperature.

What these factors are and how their values alter will be considered here, with the object of obtaining some reason for the shape of a solubility curve.

Calcium propionate furnishes a typical convex curve of solubility, and has been employed to obtain the experimental data used in this paper.

#### *The Factors which produce Equilibrium in a Saturated Solution.*

A solid may be considered to be made up of particles which by their thermal energy tend to separate, but which cohere because the attraction due to their mass, acting towards the interior, aided by the pressure of the atmosphere, counteracts the externally directed force.

In a solid which is volatile at the ordinary temperature, the opposing forces are nearly equal, but in most solids the tendency to pass into vapour is much more than counterbalanced by the force binding the particles together.

When, however, a solid is placed in a liquid, at the surface of contact an action between solid and liquid takes place of such a nature that the outwardly directed force is helped. This attraction, if strong enough, enables the particles of the solid to pass into the liquid and so form a solution, but if the attractive influence of the liquid is insufficient, the solid will not dissolve.

When solution does take place, the solid while being dissolved becomes subjected to a gradually increasing pressure as the concentration of the solution grows, due to the impact of the dissolved particles on its surface. This pressure, the osmotic pressure, acts against the forces promoting solution, and as the solid continues to pass into the liquid and this pressure increases, the disintegrating

action of the liquid on the solid lessens, the tendency of the particles to leave the solid is diminished, and finally ceases.

This is not now a state of rest but of equilibrium, for if at any point a particle passes from the solid into solution, a similar particle will leave the liquid and cohere to the solid. The solution has attained a definite concentration, it is saturated, and excess of solid can have no influence on this final state since the process of solution goes on only at the surface of the solid and the counteracting osmotic pressure is the same there at all points.

The equilibrium in a saturated solution in contact with the solid is therefore conditioned by three forces, two of which promote solution: the thermal energy of the solid tending to drive its particles apart, and the action between solid and solvent and one acting against and balancing these two: the osmotic pressure of the dissolved particles.

Alteration in the value of any one of these factors will alter the amount of solid dissolved, and change of temperature or pressure has that effect.

#### *Change of Equilibrium with Change of Temperature.*

The alteration produced on a saturated solution in contact with undissolved solid by change of temperature is best realised by considering the effect of change of temperature on each of the three forces which together produce equilibrium.

The thermal energy of the solid must always be increased by heat; work is performed against the cohesion of the particles, and their kinetic energy is augmented. This growth of disintegrating force may be proportional to rise of temperature, but it is known to increase at a greater rate than the temperature in the case of hydrated salts, especially as the point at which dehydration takes place is approached. Increase of temperature will, therefore, always raise the value of this factor and tend to facilitate solution.

The pressure exerted by the particles in solution on the undissolved solid is also increased by heat. For a constant concentration, the increase of osmotic pressure is directly proportional to the absolute temperature, but according to Nernst, with solutions of very great concentration the increase of pressure is at a somewhat faster rate.

We have, however, to consider solutions in which the concentration is not constant but changes slightly with the temperature, and it is obvious that the pressure will increase less rapidly than the law demands when the solid diminishes in solubility with heat, and more rapidly when the solubility increases with rise of temperature. It is also evident that expansion of the solution by diminishing the concentration will also lessen the osmotic pressure.

Allowing, however, for these small disturbing influences, increase of temperature will always increase the pressure on the solid and retard its solution.

The action at the surface of solid and solvent is probably chemical in its nature, therefore the force of attraction will diminish as the temperature rises, and the effect of heat will lessen the value of this solubility factor.

Equilibrium is therefore the result of a force tending to produce solution increased by rise of temperature, a force retarding solution also increased by rise of temperature, and a force promoting solution decreased by rise of temperature.

The resultant action of these three forces determines the amount of solid in solution, and a curve which represents the varying weights of solid, dissolved in a definite weight of liquid, saturated at different temperatures, will accurately represent the resultant effect of varying the temperature of the system.

Such a curve cannot be made directly, because the total amount of a solid which has passed into solution cannot be accurately found by experiment. What is really estimated is, either the weight of solid in a given volume or in a given weight of the saturated solution. In the first case, the determination at different temperatures of the concentration or the weight of solid in a given volume of the solution : values are not obtained proportional to the total weight of solid in solution unless in the hypothetical case of a solid which dissolves in a given volume of the solvent without that volume undergoing any change, and no change of bulk takes place with rise of temperature. Now, since a saturated solution has a greater volume than the solvent, and there is always an expansion by heat, with rise of temperature there will be proportionally greater amounts of substance dissolved than a curve of concentration will show.

In the second case, the estimation at different temperatures of the weights of solid in a given weight of the solution : the numbers obtained do not bear any simple relation to the amount of solid dissolved, but if from the figures obtained the weights of solid dissolved by a given weight of the solvent be calculated, then values so found are accurately proportional to the total weight dissolved at different temperatures.

This is clear from the following considerations. If a solid be placed in 10 grams of a solvent, then at any temperature when the solution has become saturated, the 10 grams, no matter what change in volume has taken place, contain all the dissolved solid. One gram or any other weight of the solvent will then always contain a quantity proportional to the total amount dissolved, and even if during the experiment some of the solvent evaporates, yet the result is not

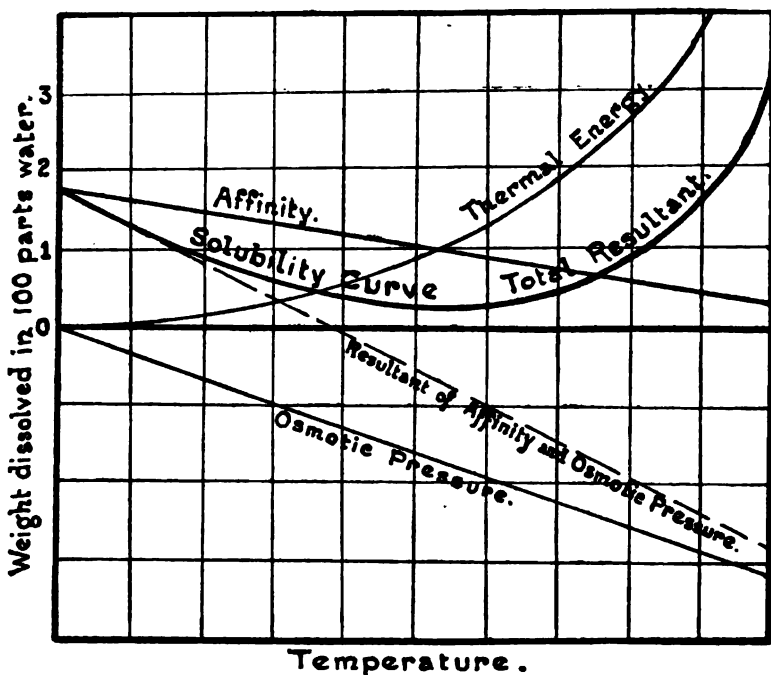


altered, since the concentration of the solution at any temperature is constant.

The ordinary solubility curve showing the weights of solid dissolved at different temperatures by 100 parts by weight of solvent is therefore the exact representation of the influence of temperature on the equilibrium between the solid and its saturated solution.

The solubility curve being the resultant of the forces producing equilibrium, it may be thought of as resolved into the component

FIG. 1.—*The component factors of a solubility curve.*



curves representing the actions of each of the forces, and it will be seen how these severally influence the shape.

On Fig. 1 is seen the solubility curve of calcium propionate and lines representing the actions of the three factors into which it might be resolved. Above the central horizontal line the values denote influences promoting solution, and below the line retarding forces.

The component due to the growth of thermal energy will be an upwardly inclined straight line if the increase is directly proportional to rise of temperature, and an upwardly inclined curve if the increase

is faster than the temperature. In the figure, a curve of the latter kind is shown.

The retarding action of the osmotic pressure may with fairness be represented by a downwardly directed line, and the affinity between solid and solvent is drawn as a line with a high value at a low temperature, decreasing in value as the temperature rises. The resultant of the affinity and osmotic pressure is shown by a dotted line, and the total resultant is the solubility curve.

A diagram of this kind is of great interest: by altering the values of the factors, all varieties of convex curves can be obtained, even one flattened to a straight line, but if the inference be true that the affinity decreases and the thermal energy and osmotic pressure increase by rise of temperature, no solubility curve concave to the temperature axis is possible.

*The Relationship between the Heat of Solution and the Shape of a Solubility Curve.*

When a given weight of solid is dissolved in a definite weight of solvent, heat is evolved or absorbed, or under certain circumstances there may be no change of temperature.

If the action between solid and solvent produces sensible heat, to that heat there must be added the heat rendered latent by the fusion of the solid and the heat of dispersion of the dissolved particles, in order to get the total heat due to the action of the solvent on the solid. Should the heat rendered latent be greater than the heat developed by combination, solution will cause a decrease of temperature, and if these two thermal effects are balanced, no change of temperature will occur.

The heat effect must, however, vary with the temperature at which solution takes place, for, remembering that forces which condition a development of heat are weakened by an increase of temperature, and those which cause an absorption of heat are strengthened, it is obvious that, with rise of temperature, the chemical action which is the cause of the heat will be weakened, whilst the physical actions will be facilitated.

At a higher temperature, therefore, the heat required to fuse the solid, and the amount of heat absorbed by the distribution of the particles, will be lessened, but if the chemical action between solid and solvent is diminished to a much greater degree, it becomes possible with the same substance to have heat evolved at a low temperature during solution, and at a higher temperature heat absorbed. Thus, if a given weight of solid and a definite weight of solvent be brought to the same temperature and mixed, heat being

evolved, at a higher temperature the physical changes may absorb all the heat due to combination, and there will be no alteration of temperature; higher still, the physical changes will require more heat than the combination gives, and a fall of temperature results, and it is not unreasonable to suppose that at a temperature where there is no action between solid and solvent, solution may take place by the thermal energy being so increased that the solid volatilises into the solvent as camphor does into air.

To test experimentally whether the heat of solution diminishes with rise of temperature, two estimations were made with calcium propionate at temperatures where it is equally soluble, one being on the descending part of the solubility curve at  $10^{\circ}$ , the other on the ascending curve at  $85^{\circ}$ .

Ten grams of crystals of calcium propionate containing 1 mol. of water were finely powdered and placed for 12 hours beside a vessel containing 25 c.c. of water. The powder was then dissolved, and the temperature rose from  $10.2^{\circ}$  to  $19^{\circ}$ . Complete solution occupied two minutes, and  $0.4^{\circ}$  was added on for loss by cooling, making the total increase  $9.2^{\circ}$ .

Next, 10 grams of the same solid were placed in a thin glass bulb with a long stem, the bulb being weighted with a little mercury. This bulb was lowered into a large test-tube containing 27 c.c. of water, and the temperature in the calorimeter raised to  $85^{\circ}$ . When the water had diminished to 25 c.c., the bulb was broken, and not more than an increase of  $1^{\circ}$  was observed. It is so difficult to get the correct heat of solution at a high temperature where the liquid has to be stirred and evaporation takes place, that exact results were impossible to obtain, but the experiment makes it sufficiently clear that the heat of solution decreases as the temperature rises, and that a negative value might even be observed at a higher part of the curve.

When a solution is nearly saturated, the heat developed by dissolving a given quantity of solid in it is much less than in a more dilute solution. The thermal effect of dissolving a given weight of solid in a given weight of water, and secondly in a nearly saturated solution of the solid made with the same weight of solvent, cannot be the same. In the latter case, although the heat developed by the chemical action will be the same, yet because of the osmotic pressure, the particle passing into solution will absorb more heat.

The following experiments show this clearly:

Four portions of 25 c.c. of water were taken, and  $2\frac{1}{2}$ , 5,  $7\frac{1}{2}$ , and 10 grams of calcium propionate placed beside them. After standing many hours at  $12.4^{\circ}$ , the several portions were mixed with the water, and the alterations of temperature noted with a delicate thermometer. The increases in temperature were respectively  $3.5^{\circ}$ ,  $6.2^{\circ}$ ,  $7.6^{\circ}$ , and

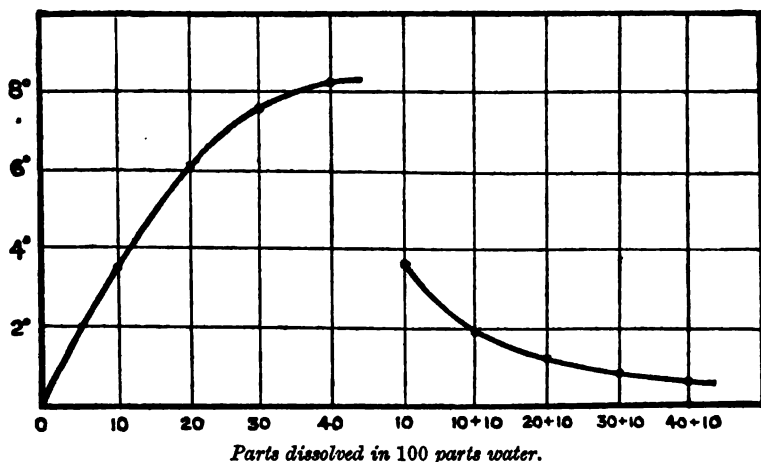
8.8°. These values, as was expected, are not proportional to the weights of solid dissolved.

The heat changes produced when the same weight of solid was dissolved in solutions of different concentrations made with the same weight of solvent were next determined.

Twenty-five grams of water and solutions, made by dissolving in 25 grams of water  $2\frac{1}{2}$ , 5,  $7\frac{1}{2}$ , and 10 grams of calcium propionate respectively, were prepared. When all the materials were cooled to 12.4°,  $2\frac{1}{2}$  grams of solid were added to each vessel. Increases of 3.5°, 2°, 1.4°, 0.9°, and 0.6° were obtained. These results are shown graphically on Fig. 2.

Thus the more concentrated the solution, the less the amount of sensible heat evolved when a given weight of solid is dissolved in it,

FIG. 2.—Heat of solution of calcium propionate.



and if solution can be continued so that a supersaturated solution is produced, absorption of heat may take place. Thus Reicher and Deventer (*Zeit. physikal. Chem.*, 1890, 5, 559) state that cupric chloride dissolves in water with evolution of heat, but that in a completely saturated solution it dissolves with reduction of temperature.

This heat of solution in a saturated solution can be experimentally found, for if a supersaturated solution be made at a certain temperature, changed to another temperature, and the excess of solid separated out by dropping in a crystal, the amount of heat absorbed by a solution supersaturated at a low temperature, or the amount of heat evolved from a solution supersaturated at a high temperature, will be the same as that evolved or absorbed respectively by the solution of the separated solid if the solution could take place in a saturated solution.

The solubility curve represents only the heat changes which will be produced by dissolving a particle of solid in a solution nearly saturated.

Considering a curve like that of calcium propionate, and starting from the point of least solubility, if the temperature is raised the solution becomes unsaturated, solid passes into solution, and heat is absorbed; if the temperature is lowered, solid also passes into solution and again heat is absorbed. A downward curve will therefore indicate evolution, and an upward curve absorption, of heat when a particle of solid finally saturates the solution.

When, however, a solution is dilute, even if the temperature is above that of the least solubility, the addition of solid still causes an evolution of heat. The statement which is generally made that if a solid when placed in water dissolves with evolution of heat it will diminish in solubility with rise of temperature, is only partially true; the solubility curve indicates only the sign of the heat of solution in a nearly saturated solution.

#### *The Influence of Pressure on the Equilibrium in a Saturated Solution.*

When pressure is applied to a saturated solution in contact with the solid, the effect will be different according as the total volume of solid and liquid is greater or less after solution than before.

If the solid *plus* the solution has a greater volume than the solid *plus* the solvent, that is, if there is an expansion during solution, external pressure tending to diminish the volume increases the osmotic pressure by increasing the concentration in a greater ratio than the thermal energy of the solid is increased by compression, particles return to the solid and the amount of substance in solution is diminished.

If, however, the solid *plus* the solution has a smaller volume than the solid and solvent, the external pressure tending to diminish the volume helps the solution of the solid and the concentration of the liquid increases.

Thus the pressure helps most the forces which tend to cause a diminution of volume and alters the equilibrium in the direction in which these forces act.

Experimental proofs of these facts have been given by Sorby (*Proc. Roy. Soc.*, 1863, 12, 538) and Braun (*Ann. Phys. Chem.*, 1887, 30, 250), and in addition Braun showed from thermodynamical considerations that with the same pressure the sign of the heat of solution would influence the amount of solid dissolved.

When, therefore, the solubility curve is convex and the heat of solution in a saturated solution changes from positive to negative with rise of temperature, the effect of pressure considered apart from any change of volume will be different at different parts of the curve.

No data are available for the volumes of solid and saturated solution of a substance like calcium propionate at various temperatures, and the true change of equilibrium by change of pressure cannot be followed.

The effects of small changes of pressure are, however, so slight that in considering the shape of a solubility curve they may be neglected.

### *Compound Solubility Curves.*

From the foregoing considerations, it is obvious that the forces at work during solution slowly change their values with rise of temperature, and the resultant curve for the same substance must be an unbroken line.

If a solubility curve shows one or more breaks, the points of flexure are the meeting places of curves representing the solubilities of different hydrates, which are physically different substances.

Experiment proves this to be the case: no broken curve is obtained for a substance which cannot change in composition with the temperature. If an anhydrous salt is in contact with the solvent at a low temperature, the solubility curve will be unbroken; if the solid contains water of crystallisation the curve is broken or simple, according as the substance in contact with its saturated solution loses water or not in the range of temperature employed.

The point of flexure is neither the end of one curve nor the beginning of the next curve; it is simply a place of meeting. The lower temperature curve may, under favourable conditions, be continued above the transition point, and the higher temperature curve can pass below it, but the equilibrium is then unstable, and it is experimentally difficult to prevent change to the more stable solid.

The condition of equilibrium at a transition point is interesting: two solids are there in equilibrium with the same solution, the sums of the thermal energy and affinity in both are therefore equal, since they are both subjected to the same osmotic pressure. From the point of view of the "phase rule," it is a non-variant equilibrium; two components are present: the solid and water, and there are four phases: one liquid, one vapour, and two solid. There is no degree of freedom, and any change of temperature or pressure destroys one of the solid phases, producing a mono-variant system.

It is probable that all solubility curves which have been drawn, showing a continuous bend concave to the temperature axis, should be two curves. The observer, when joining the points found experimentally, has missed the transition point.

This is the case with barium acetate, the solubility of which was determined by Tilden and Shenstone (*Phil. Trans.*, 1884, 174, 23) and the curve is figured in several books (*Ostwald's Lehrbuch*, vol. i.).

I have found that there is no concave part on this curve, and that the investigators by estimating the solubility only at points widely apart, and neglecting to analyse the solid in contact with the solution, joined points on two different curves and cut off the transition point.

Another case is that of calcium isobutyrate, where Chancel and Parmentier missed the meeting point of the two curves shown on Fig. 4 in the preceding paper.

From theoretical considerations, it would seem that the existence of solubility curves concave to the temperature axis was improbable, and in all cases where concave curves have been carefully examined they have been shown to be due to two substances, the exact point of mutual equilibrium of which had been missed.

Summing up, we have found that there are three factors which condition the solubility of a substance: the affinity of solid and solvent, the thermal energy of the solid, and the pressure of the dissolved particles, and that the values of these vary with temperature and pressure.

When equilibrium is attained, a solution is saturated, and a curve of solubilities is an exact representation of the resultant of the solubility factors at varying temperatures. If the values of the factors vary directly with the temperature, the solubility curve is a straight line; when the change is at a different rate, a curve is obtained. No well authenticated case of a solid the solubility of which is represented by a curve concave to the temperature axis is known, and the normal shape is either a straight line or a convex curve.

Many calcium salts have solubility curves which descend with rise of temperature, reach a minimum, and then ascend, but other substances have solubilities represented by portions of such a curve. It will depend on the relative values of the solubility factors, and on the range of temperature over which the estimations have been made, whether a curve will descend and rise, or descend only, or as is most commonly the case be an ascending curve.

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XXXVI.—*Enzyme Action.*

By ADRIAN J. BROWN.

*Introduction.*

IN a paper on the fermentative functions of yeast (Trans., 1892, 61, 380), the author described some experiments which showed that the character of the action of fermentation differed in a very marked manner from the character of the action usually attributed to enzyme change.

The author's experiments indicated that during fermentative change a constant amount of yeast decomposes an approximately *constant weight* of sugar in unit time in solutions of varying concentration, and that the velocity of fermentative action is therefore represented graphically by a *straight line*. On the other hand, the character of the action usually attributed to an enzyme is that a constant amount of the ferment changes in unit time a *constant fraction* of the reacting substance present, and that the velocity of its action is represented by the *logarithmic curve* of mass action.

At the time the author's work (*loc. cit.*) was published, the fermentative power of the yeast cell was considered to be a life function inseparable from the cell, and there appeared to be nothing specially remarkable in the observation that fermentation, a life function, differed in the velocity of its action from enzyme action. But since the more recent work of Buchner has demonstrated that the phenomenon of fermentation is caused by enzyme action, the question assumed another aspect. If fermentation is now regarded as an enzyme action, then, either the velocity of its action must be regarded as differing essentially from that which is usually attributed to other enzymes, or the experimental evidence on which the assumed difference rests must be regarded as misleading.

It was with the intention of investigating this question that the author commenced the work described in the following paper.

*Velocity of the Action of Fermentation.*

If the view is adopted as a working hypothesis that the supposed difference in velocity of the actions of fermentation and ordinary enzyme change does not exist, but that it is due to some misconception, it is evident misconception may have arisen concerning either the velocity of fermentation or that of ordinary enzyme change, and consequently a re-examination of the experiments by which both velocities have been determined appeared desirable.



As the author is responsible for the experiments by which the velocity of fermentation has been determined, he commenced his investigations by repeating them. It does not appear necessary, however, to give the results of this work, for the experiments were similar to those described in the earlier paper (*loc. cit.*), and the results fully confirmed the conclusion that fermentative action does not proceed in accordance with the law of mass action.

As the general character of the action of fermentation appeared to be thus established, the author proceeded to examine the experimental evidence from which the conclusion is drawn that the velocity of enzyme action accords with the law of mass action.

### *Velocity of Enzyme Action.*

The generally accepted view regarding the velocity of enzyme action is based on the researches of Cornelius O'Sullivan and F. W. Thompson on the action of invertase on cane sugar (*Trans.*, 1890, 57, 865). These authors demonstrated the velocity of the action of invertase in the following manner.

Invertase was caused to act in solutions of cane sugar, and during the progress of the actions the quantities of sugar inverted during a succession of time intervals were determined. By this means, observations were obtained from which time curves were constructed which represented graphically the velocity of the action of inversion. When these curves were compared with the curve representing simple mass action, a very close agreement in shape was observed, which appeared to indicate that they were of the same order, and from this close agreement in shape, C. O'Sullivan and Thompson concluded that the action of invertase instanced the operation of the law of mass action.

This conclusion has also received confirmation from the researches of James O'Sullivan on the power of inversion of living yeast cells (*Trans.*, 1892, 61, 926), the experiments of this author indicating that the velocity of action of the living cell is the same as that of the extracted invertase used by C. O'Sullivan and Thompson in their experiments.

The evidence referred to is, so far as the author is aware, all that has been brought forward to support the conclusion that the velocity of enzyme action indicates the operation of a simple mass action.

Hitherto, no doubt, the want of additional evidence has not been felt, owing to C. O'Sullivan and Thompson's experiments appearing conclusive so far as invertase is concerned, and also to the fact that the conclusion these authors arrived at with regard to the character of enzyme action is one which there is every reason to anticipate.

But when the character of the action of fermentation, now very generally recognised as an enzyme action, was found to differ essentially from that attributed to invertase both in the free state and within the living yeast cell,\* it raised doubt in the author's mind regarding the accuracy of C. O'Sullivan and Tompson's conclusion. Moreover, the author found that he was not alone in his distrust, for it has already been pointed out by Duclaux, in a criticism on C. O'Sullivan and Tompson's work (*Ann. Inst. Pasteur*, 1898, 12, 96), that the logarithmic curve representing the action of invertase, on which C. O'Sullivan and Tompson founded their conclusion, may be shaped by other causes than the supposed action of mass. For Duclaux maintains that such a curve represents, not only a decrease in a changing substance, but also, and equally well, an increase in the products of change, and it is possible these products of change may act as the influence shaping the curve and not the influence of mass action. No experimental evidence sustaining this point is, however, brought forward by Duclaux.

As C. O'Sullivan and Tompson's conclusion rests entirely on the shape of the curve representing the action of invertase, the author considered it advisable first to repeat the experiments from which the curve was derived. Conditions of experiment similar to those used by C. O'Sullivan and Tompson were employed, but the invertase used was prepared in a different manner from the enzyme with which these authors experimented.

C. O'Sullivan and Tompson worked with invertase obtained from an extract of auto-digested yeast by precipitation with alcohol, and in so doing encountered the difficulty that the action of invertase prepared in this manner was very irregular unless it was associated with a small quantity of sulphuric acid. Moreover, the amount of acid required to reach the point described by these authors as "the most favourable condition of acidity," at which point it was necessary to work, varied in every experiment in a most remarkable manner.

It appeared very desirable to avoid this complication when repeating C. O'Sullivan and Tompson's experiments, so the author employed in his experiments an extract of invertase prepared from dried yeast by digestion with water. An extract of invertase prepared in this manner was quite suitable for the purpose of the experiments, and the risk of modifying the activity of the invertase by precipitation was avoided. That this method of obtaining a preparation of invertase suitable for experiment was preferable to that employed by C. O'Sullivan and Tompson was evidenced by the invertase being free from the irregularities of action associated with the precipitated in-

\* Presumably, invertase within the wall of the living cell is in the same position as zymase with regard to its action as an enzyme.

vertase used by these authors, and, in consequence, it could be employed without the complicating addition of sulphuric acid.

The author's experiments, like those of C. O'Sullivan and Thompson, consisted in the addition of a suitable amount of invertase solution to a solution of cane sugar, and in determining, by means of a polarimeter, the fractions of the sugar inverted during successive intervals of time.

Instead, however, of expressing the velocity of the inversion change by means of a curve, the author preferred to make use of the value  $k$ , derived from the expression  $\frac{1}{\theta} \log \frac{1}{1-x}$ . This well-recognised means of expression, usually adopted now to demonstrate such changes as those of a mass action, has the advantage of avoiding certain difficulties which attend the comparison of calculated and experimental curves.

The results of two series of experiments determining the velocity of the action of invertase are given in Tables I and II :

TABLE I.—*Velocity of inversion change in 9.48 per cent. solution of cane sugar. 500 c.c. of solution of sugar and 25 c.c. of invertase solution used. Temp. 30°.*

Duration of time interval in minutes. $\theta$ .	Fraction of sugar inverted in $\theta$ . $x$ .	$k = \frac{1}{\theta} \log \frac{1}{1-x}$ .
30	0.265	0.00445
64	0.509	0.00483
120	0.794	0.00571
180	0.945	0.00698
240	0.983	0.00787
300	1.003	

During the course of a change proceeding as a simple mass action, it is well known that the value  $k$ , determined for any point of the action, is a constant. But in the experiments described in the above tables it will be noticed that the value  $k$  increases in both experiments as inversion proceeds, until the value at the termination of the experiments is about 70 per cent. higher than at the beginning.\*

Now, these results do not support the view that the action of inversion instances a mass action, as C. O'Sullivan and Thompson believed, for they differ very materially from the results these authors obtained. But in order to emphasise more distinctly the difference between the

\* It will be noticed that there is no indication of "reversion" in these inversion experiments. An increase in the value of  $k$  denotes an increasing velocity; reversion would lead to a decreasing velocity.

TABLE II.—*Velocity of inversion change in 19.28 per cent. solution of cane sugar. 500 c.c. of sugar solution and 25 c.c. of invertase solution used. Temp. 30°.*

Duration of time interval in minutes. $\theta$ .	Fraction of sugar inverted in $\theta$ . $x$ .	$k = \frac{1}{\theta} \log \frac{1}{1-x}$ .
30	0.180	0.00201
64	0.256	0.00201
120	0.454	0.00219
180	0.619	0.00232
240	0.738	0.00242
300	0.831	0.00257
360	0.890	0.00265
420	0.935	0.00283
480	0.961	0.00293
540	0.983	0.00327
581	0.990	0.00344

character of the action of inversion and that of a mass action, the results of an experiment involving mass action are given in Table III for the purpose of comparison. In this experiment, the author employed sulphuric acid to invert cane sugar, and thus obtained results from a typical mass action, which are directly comparable with those effected by invertase.

TABLE III.—*Velocity of inversion change of cane sugar by acid. 600 c.c. of a 20 per cent. solution of cane sugar, and 35 c.c. of normal  $H_2SO_4$  used. Temp. 48°.*

Duration of time interval in minutes. $\theta$ .	Fraction of sugar inverted in $\theta$ . $x$ .	$k = \frac{1}{\theta} \log \frac{1}{1-x}$ .
30	0.165	0.00261
61	0.317	0.00271
90	0.433	0.00274
120	0.532	0.00275
150	0.617	0.00278
180	0.688	0.00281
243	0.785	0.00275
302	0.856	0.00279
362	0.902	0.00278
		Mean } 0.00275 result }

The above experiments show very clearly, when a true mass action is followed under experimental conditions similar to those used when determining the character of the action of invertase, that a very differ-

ent result is obtained. The small and irregular variation in the value of  $k^*$  is very different from the regular and well marked increase in the value of  $k$  observed in the experiments with invertase given in Tables I and II, and from this there can remain but little doubt that the order of progression of inversion differs essentially from that of a mass action. At present, the author has not attempted to determine any expression for the order of progression of inversion under the conditions of his experiment, because, for the immediate purpose of his investigation, it is only necessary to show that inversion does not proceed as a mass action.†

Although the author's experiments throw the greatest doubt on the accuracy of the conclusion that inversion evidences mass action, they cast very little light on the true character of the action of invertase, and in order to obtain more knowledge, it became necessary to adopt some method of experiment different from that which has already been described.

\* The variations in value of  $k$  are no doubt due to experimental error. Very slight changes in temperature have a marked influence on the velocity of inversion change by acid.

† Since writing the above, a communication from Victor Henri has been published (*Compt. rend.*, 1901, 133, 891) on the velocity of inversion change. This author arrives at the conclusion that the action proceeds in accordance with the expression  $2k_1 = \frac{1}{\theta} \log \frac{1+x}{1-x}$ .

On applying this purely mathematical expression of velocity to the inversion experiments described in Table II, the following results have been obtained:

TABLE II.—*Recalculated.*

Duration of time interval in minutes. $\theta$ .	Fraction of sugar inverted in $\theta$ . $x$ .	$2k_1 = \frac{1}{\theta} \log \frac{1+x}{1-x}$ .
30	0.130	0.00376
64	0.256	0.00355
120	0.454	0.00356
180	0.619	0.00346
240	0.738	0.00343
300	0.831	0.00353
360	0.890	0.00343
420	0.935	0.00351
480	0.961	0.00354
540	0.983	0.00383
581	0.990	0.00395

It will be observed from the remarkably close agreement of the numbers in the third column, representing the values  $2k$ , that the author's experiments indicate a very similar velocity for inversion change to that which is represented by Henri's expression. This is of interest as further assisting to establish the fact that the progress of an inversion change is not ordered in conformity with the law of mass action.

Such a method exists in causing a constant amount of invertase to act on varying amounts of cane sugar in constant volume of solution for a constant brief interval of time. Under these conditions, the variable in the actions is the amount of reacting substance (cane sugar) present, and in a simple mass action under these conditions, the amount of reacting substance changed in unit time is a *constant fraction* of the reacting substance present.\*

In Table IV, the results of a series of five experiments are given in which a constant amount of invertase has acted on varying amounts of sugar under the conditions just named :

TABLE IV.—*Inversion changes by a constant amount of invertase acting in constant volume of cane sugar solutions of varying concentrations, in constant time. 1 c.c. of invertase solution added to 100 c.c. of cane sugar solution in each experiment. Temp. 28°.*

No. of experiment.	Grams cane sugar per 100 c.c.	Grams cane sugar inverted in 60 minutes.	Fraction of cane sugar inverted in 60 minutes = $x$ .	$k = \frac{1}{\theta} \log \frac{1}{1-x}$ .
1	4.89	1.230	0.252	0.00210
2	9.85	1.355	0.138	0.00107
3	19.91	1.355	0.068	0.00051
4	29.96	1.235	0.041	0.00031
5	40.02	1.076	0.027	0.00020

When the law of mass action was evidenced by Ostwald's experiments on methyl acetate (*loc. cit.*) under conditions similar to those employed in the above experiments, he found that a *constant fraction* of the methyl acetate present in each solution was hydrolysed in unit time, and therefore, if the action of invertase is an instance of simple mass action, a *constant fraction* of the cane sugar present in each of the above experiments should be inverted. But it will be noticed that instead of a constant fraction, a constant (or approximately constant) *weight* of the cane sugar is inverted. The fraction inverted diminishes in inverse proportion to the amount of cane sugar present in the experiments, and, as a consequence, the value  $k$ , which is constant in a true mass action, varies to a very large extent.

These experiments,† therefore, confirm the conclusion derived from the experiments given in Tables I and II, that the influence of

\* For experimental confirmation of this necessary consequence of mass action, see Ostwald on the hydrolysis of methyl acetate by hydrochloric acid ("Outlines of General Chemistry," p. 353).

† Duclaux (*loc. cit.*) quotes some experiments with invertase derived from *Aspergillus niger* which fully confirm the author's experiments described in Table IV.

mass action does not rule in inversion change. Moreover, when the velocity of the action of inversion determined in the manner described in Table IV is examined, it will be noticed that the action is similar in character to that of fermentation, referred to at the commencement of this paper. During alcoholic fermentation, a constant amount of yeast decomposes in unit time an approximately *constant weight* of sugar in equal volumes of solution containing varying amounts of sugar. Invertase is now found to invert approximately constant quantities of cane sugar under similar conditions. Therefore the supposed difference in character of the two actions of fermentation and inversion which led the author to commence the investigation described in this paper does not exist, for the action of both, if expressed graphically, is represented approximately by a straight line. So far, therefore, the first object of the investigation is attained.

Although experiments carried out in the manner just described show that the general character of the action of invertase resembles that of fermentation, they do not explain the apparent paradox that when the action of invertase is studied during a series of consecutive changes in a single solution, the velocity of the action is then represented, not by a straight line, but by a curve, showing that there is a decrease in the *absolute amount* of sugar inverted during each time interval (see the experiments in Tables I and II and foot-note to p. 378 which indicate that, although the curve of the action is not so pronounced as the logarithmic curve of mass action, it is still very marked).

Apparently there are two causes which may lead to the production of such a curve during the continued action of invertase in a solution of cane sugar. Either it may be due to a natural weakening of the invertase by continued work,\* or it may be due, as Duclaux has suggested (*loc. cit.*), to the action of invertase being influenced prejudicially by the accumulation of its own products of inversion. From what is known regarding the very large amount of cane sugar which is capable of being hydrolysed by a very small amount of invertase, the former cause appeared to be far less probable than the latter, so the author turned his attention to the investigation of the possible retarding influence of inversion products on the action of invertase.

#### *Action of Inversion Products on the Velocity of Inversion Change.*

The method of experiment adopted by the author was to observe the action of a constant amount of invertase during a brief interval of time in equal volumes of solutions containing a constant amount of

\* Some interesting experiments of Victor Henri (*loc. cit.*) indicate that sustained work does not weaken the action of invertase,

cane sugar and varying amounts of invert sugar. The invert sugar used in the experiments was prepared by the action of invertase on a concentrated solution of cane sugar until complete inversion was obtained, the invertase being then destroyed by raising the temperature of the solution to 90°.

The following table gives particulars of a series of experiments in which different amounts of this solution of invert sugar were mixed with a constant amount of cane sugar solution, the total volumes of the solutions in the different experiments being made constant:

TABLE V.—*Influence of invert sugar on the action of invertase. Volume of each experiment, 100 c.c. 1 c.c. of invertase solution used in each experiment. Time of change, 80 minutes. Temp. 30°.*

No. of experiment.	Grams cane sugar present in 100 c.c.	Grams invert sugar present in 100 c.c.	Grams cane sugar inverted in 80 minutes.
1	4.06	none	2.27
2	4.06	1.47	2.21
3	4.06	5.39	1.99
4	4.06	11.88	1.66
5	4.06	17.87	1.25

In these experiments, if the presence of invert sugar exerted no influence on the action of invertase, the quantities of cane sugar inverted in constant time would be constant, for the same quantities of cane sugar and invertase were present in all the experiments. But an examination of the table shows that the amount of cane sugar inverted decreased as the quantity of added invert sugar increased, until, in the last experiment (No. 5), the quantity of cane sugar inverted has been reduced to nearly one-half in the presence of 17.87 grams of invert sugar.

The series of experiments indicate, therefore, that the presence of invert sugar has diminished the activity of invertase, and that the arresting influence has increased as the amount of invert sugar has increased. But it is possible that the arresting influence of invert sugar may be due, not to the presence of the sugar as such, but to the increased viscosity of the solution containing it, for, owing to the manner in which the experiments were conducted, the total amount of sugars in the different solutions is an increasing one from the first to the last experiment. In order to investigate this question, a series of experiments was conducted in a similar manner to those described in Table V, excepting that lactose was used in the place of invert sugar. Lactose is a sugar which is not changed by the action of invertase, but its solutions possess a viscosity almost identical with that of solutions



of invert sugar of similar concentrations. Therefore in a series of experiments with lactose in place of invert sugar, the factor of increasing viscosity is introduced apart from any special influence possessed by invert sugar alone.

The results of a series of experiments with lactose are given below :

TABLE VI.—*Influence of lactose on the action of invertase. Volume in each experiment, 100 c.c. 1 c.c. of invertase solution used. Time of change, 60 minutes. Temp. 28°.*

No. of experiment.	Grams cane sugar present in 100 c.c.	Grams lactose present in 100 c.c.	Grams cane sugar inverted in 60 minutes.
1	7.0	none	2.072
2	7.0	5.0	2.052
3	7.0	10.0	2.052
4	7.0	20.0	1.893

The results given in this table show that the influence on the action of invertase of the viscosity (or any other property) of the lactose used in the experiments is comparatively insignificant. In experiments 2 and 3, the retarding influence of 5 per cent. and 10 per cent. of lactose lies almost within the limits of experimental error, and in 4, in which the large amount of 20 per cent. lactose is present, the reduction in the amount of cane sugar inverted is only 9 per cent. On the other hand, it has already been shown (Table V, No. 4) that 17.8 per cent. of invert sugar under similar conditions reduced the amount of cane sugar inverted to the extent of 45 per cent. The major part of this reduction, therefore, is not due to viscosity, but must be occasioned by the arresting influence of invert sugar as such.

When the arresting influence of invert sugar on the action of invertase is thus established, there is then no difficulty in explaining the apparent paradox that the true action of invertase, which is indicated graphically by a straight line, is expressed by a curve when the action is determined for a series of progressive changes in one solution. Under the latter conditions, as the action of inversion proceeds, the products of inversion accumulate, and these consequently exert an increasing retarding influence on the action of inversion, and thus compel the action to follow the course of a curve.

*The Inversion Functions of Living Yeast Cells.*

So far, when discussing the action of invertase, the author has referred more especially to C. O'Sullivan and Tompson's experiments and conclusion regarding the velocity of its action. It now remains to discuss J. O'Sullivan's experiments, alluded to at the commencement of this paper as supporting C. O'Sullivan and Tompson's conclusion.

It will be remembered that J. O'Sullivan, when studying the velocity of the inversion change produced by living yeast in solutions of cane sugar (*loc. cit.*), found that the value  $k$  derived from the expression  $\frac{1}{\theta} \log \frac{1}{1-x}$ , was constant, or nearly so, during the progression of the changes, and from this he concluded that the velocity of change followed the law of mass action.

There is no doubt that J. O'Sullivan's determinations—like those of C. O'Sullivan and Tompson—indicate a velocity approximating to that of mass action, when the progress of an inversion change is followed in one solution; but J. O'Sullivan has overlooked the fact—rendered evident by his own determinations—that, although the velocity in each separate change approximately follows the law, the value  $k$  found for comparable experiments in which varying amounts of sugar have been used, shows that there is no conformity with mass action, but, on the contrary, indicates that a *constant amount* of sugar is inverted—an action similar to that which has been shown for free invertase.

For instance, in J. O'Sullivan's paper four comparable experiments are described, in which equal amounts of yeast were used in equal volumes of solution during equal intervals of time, the only variable being the quantity of cane sugar present in the solutions. The results of these experiments are given in the table on p. 384.

It will be noticed, on examining this table, that J. O'Sullivan has determined the progression of inversion in each of the four solutions at three time intervals, and the values of  $k$  for the changes in each separate solution are fairly constant; but the values  $k$  should also be constant for all four of the solutions if the velocity of change follows the law of mass action, because the solutions only differ in containing varying quantities of sugar. On the contrary, however, the value  $k$  varies inversely as the amount of sugar present, in a similar manner to the value  $k$  in the author's experiments with invertase, given in Table IV.

■ A similar conclusion may also be derived from the numbers in the column in Table VII showing the fractions of cane sugar inverted during the experiments. If the first numbers in each series are

TABLE VII.—*Velocity of inversion by living yeast cells (J. O'Sullivan).*

Grams cane sugar per 100 c.c.	Grams of yeast used.	Time of action in minutes. $\theta$ .	Fraction of sugar inverted. $x$ .	$k = \frac{1}{\theta} \log \frac{1}{1-x}$ .
5	0.5	30	0.1636	0.0025
		60	0.3164	0.0027
		120	0.5442	0.0028
10	0.5	30	0.1042	0.0016
		60	0.1544	0.0012
		120	0.2780	0.0012
20	0.5	30	0.0627	0.0009
		60	0.0850	0.0006
		120	0.1467	0.0006
30	0.5	30	0.0366	0.0005
		60	0.0495	0.0003
		120	0.0662	0.0003

compared, it will be noticed that the fractions inverted are, approximately, in inverse proportion to the amounts of cane sugar present in the solutions—or, in other words, the actual *quantity* of sugar inverted is the same for all the experiments.

Thus J. O'Sullivan's experiments show that the velocity of action of the inversion function of yeast falls into line with the action of free invertase, and the action of fermentation,\* previously demonstrated by the author.

#### *Time and Molecular Change.*

It was stated at the commencement of this paper that the author's object was to examine, and, if possible, bring together, certain conclusions regarding the nature of enzyme action which seemed to be contradictory. Experimental evidence appeared to show that on the one hand the action of invertase, both in the free state and confined within the living cell, followed the law of mass action; and, on the other hand, that the action of the enzyme of alcoholic fermentation followed a different law. The author has now shown that these supposed differences in character of action do not exist, and that the actions of both inversion and fermentation follow approximately

\* It is interesting to note the agreement in character of action of the inversion and fermentation functions of the *living yeast cell*, as it tends to strengthen the conclusion that fermentation is a true enzyme action.

the same order of progression—an order which is not that of mass action.

But this conclusion, that the actions of the two enzymes exhibit an exceptional order of progression differing from that of mass action, introduces a question which requires explanation.

It appears impossible to believe that enzyme change, however produced, is independent of mass action. According to our present conception of matter and its mechanics, such an idea appears to be inconceivable. Therefore, in looking for some explanation of the exceptional character of the actions of inversion and fermentation, the author concludes that the influence of mass in these actions, as they have been studied so far, must be limited or concealed by some other influence.

If such an influence is looked for, consideration shows that it may be due to the existence of a time factor in certain forms of complex molecular change.

When the law of mass action regulating simple chemical change has been confirmed by direct experiment, the reactions investigated have been changes such as the hydrolysis of methyl acetate by hydrochloric acid (Ostwald, *loc. cit.*) and the inversion of cane sugar by acids. In such experiments, the molecular change following collision of the reacting molecules takes place with extreme rapidity and the existence of a time factor is not in evidence in experimental determinations of the velocity of change. But it is quite conceivable, with regard to such a change as that of enzyme action, that the time elapsing during molecular union and transformation may be sufficiently prolonged to influence the general course of the action.

There is reason to believe that during inversion of cane sugar by invertase the sugar combines with the enzyme previous to inversion. C. O'Sullivan and Tompson (*loc. cit.*) have shown that the activity of invertase in the presence of cane sugar survives a temperature which completely destroys it if cane sugar is not present, and regard this as indicating the existence of a combination of the enzyme and sugar molecules. Wurtz (*Compt. rend.*, 1880, 91, 787) has also shown that papain appears to form an insoluble compound with fibrin previous to its hydrolysis. Moreover, the more recent conception of E. Fischer with regard to enzyme configuration and action, also implies some form of combination of enzyme and reacting substance.

Let it be assumed, therefore, that one molecule of an enzyme combines with one molecule of a reacting substance, and that the compound molecule exists for a brief interval of time during the further actions which end in disruption and change. Let it be assumed also that the interval of time during which the compound molecule of enzyme and reacting substance exists is  $1/100$  of a time unit.

Then it follows that a molecule of the enzyme may assist in effecting 100 completed molecular changes in unit time, but that this is the limit to its power of change.

Again, let it be assumed that the number of molecular collisions between the active and reacting molecules which lead to their combination bears some proportion to the number of possible completed molecular changes in unit time. Let the number of collisions be 20, then there may be 20 complete molecular changes; if 40, there may be 40 changes. In fact, the action of the mass law is observed, for other conditions being equal, the average number of molecular collisions must depend on the number of molecules, or mass, of the matter present.

But now assume that the mass of reacting substance is increased, so that the number of molecular collisions in unit time exceeds 100; let it be 150, 1000, or any other number larger than 100. Then, although the number of molecular collisions may exceed 100 by a number following the law of mass action, 100 molecular changes cannot be exceeded, for the compound enzyme and sugar molecule is only capable of effecting 100 complete changes in unit time.

It follows, therefore, that if, in a series of changes like the imaginary ones described, a constant amount of enzyme is in the presence of varying quantities of a reacting substance, and in all cases the quantity of reacting substance present ensures a greater number of molecular collisions in unit time than the possible number of molecular changes, then a *constant weight* of substance may be changed in unit time in all the actions.

When invertase acts in solutions of cane sugar of varying concentrations, an approximately *constant weight* of sugar is inverted in unit time, and the yeast cell, under similar conditions, ferments an approximately *constant weight* of sugar; it appears, therefore, that the exceptional character of these changes may be satisfactorily accounted for by the theory advanced.

Experimental evidence may also be brought forward in support of this theory.

In Table IV, the results of the author's experiments show that approximately constant quantities of cane sugar are inverted in unit time in solutions varying in concentration from 5 to 40 per cent. If the results of these experiments are looked at in the light of the author's theory, the number of molecular collisions in unit time in each experiment must have equalled, or exceeded, the possible number of changes by the compound molecule of enzyme and sugar. But this has happened in solutions containing 5 per cent. and upwards of cane sugar. It must, however, be possible to make solutions of varying quantities of cane sugar so dilute that the number of molecular collisions taking place in unit time between the sugar molecules and a

constant number of invertase molecules will fall below the possible number of changes. Then, if the author's theory be correct, the progress of inversion in a series of these dilute solutions of cane sugar of different concentrations will exhibit an action in accordance with the law of mass action, for the time interval of change no longer restricts its effect.

It seemed very possible when commencing the attempt to demonstrate this experimentally that it might prove that the solutions of cane sugar required for the purpose were too dilute to use for experimental purposes. But when the attempt was made, it was found that the necessary dilutions are within the limit of experiment, as the results given in the following table (VIII) show :

TABLE VIII.—*Velocity of action of invertase in very dilute solutions of cane sugar. 100 c.c. of cane sugar solution and 1 c.c. of diluted invertase solution employed for each experiment. Time of change, 60 minutes. Temp. 31°.*

No. of experiment.	Grams cane sugar per 100 c.c.	Grams cane sugar inverted in 60 minutes.	$k = \frac{1}{\theta} \log \frac{1}{1-x}$
1	2.0	0.808	0.00182
2	1.0	0.249	0.00219
3	0.5	0.129	0.00239
4	0.25	0.060	0.00228

The results given in the above table furnish very strong evidence in support of the view that in the dilute solutions of cane sugar employed the number of contacts of the sugar molecules with the invertase molecules in unit time have been reduced to a less number than the possible number of molecular changes. In experiment No. 1, in which a concentration of 2 grams of sugar per 100 c.c. has been used, the dilution appears to have been hardly sufficient to reach the desired point. In Nos. 2, 3, and 4, however, the quantities of sugar inverted in unit time are no longer constant quantities—as was found in the experiments with concentrations of 5 per cent. and upwards, given in Table IV., and decrease in direct proportion with the concentrations.

Moreover, the value  $k$  in these experiments is a constant number.

These observations indicate a change in accordance with mass action, which, according to the author's theory, should be evidenced in solutions of sufficient dilution. There is, therefore, reason to believe from the results of the above experiments that the exceptional action of inversion in all but very dilute solutions of cane sugar is due to a time

factor accompanying molecular combination and change which limits the influence of mass action.

It has been shown in this paper that the action of alcoholic fermentation follows approximately the same order of progression as that of inversion, and the work of Kastle and Loevenhart (*Amer. Chem. J.*, 1900, 24, 491) shows that the action of lipase progresses in the same manner; it therefore appears probable that both these enzyme actions are regulated, like inversion, by a time factor accompanying complex molecular change.

It will be noticed that the author's theory demands, not only the formation of a molecular compound of enzyme and reacting substance, but the existence of this molecular compound for an interval of time previous to final disruption and change. Various speculations regarding the conditions ruling such an effect suggest themselves, but the author does not at present attempt to discuss this question.

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### XXXVII.—*The Velocity of Hydrolysis of Starch by Diastase, with some Remarks on Enzyme Action.*

By HORACE T. BROWN, LL.D., F.R.S., and T. A. GLENDINNING, F.I.C.

THE experimental work here described, on the rate of change during the hydrolysis of starch by malt diastase, was completed more than four years ago, but the results were temporarily put on one side, owing to the impossibility of reconciling them with the views then current with regard to the analogous changes induced by the action of invertase on cane sugar.

The investigations of C. O'Sullivan and Tompson (*Trans.*, 1890, 57 834) and of J. O'Sullivan (*Trans.*, 1892, 61, 926) had led these observers to conclude that the time rate of change during the inversion of cane sugar by the enzyme is the same as that observed in acid hydrolysis; that it conforms, in fact, to the logarithmic formula characteristic of a unimolecular reaction.

Our own observations on the hydrolysis of starch by diastase had convinced us that the rate of change certainly does not conform to this simple law of mass action, but that there is a progressive increase in the value of the "velocity coefficient" which appears at first sight to differentiate the mode of action of diastase from that of invertase. The recent work of Adrian Brown and of V. Henri has shown, however,

that in cane sugar hydrolysis, both as regards the time elements of change and the influence of varying concentration, the action of the enzyme differs materially from that of dilute acids.

This has led us to re-examine our experiments on starch hydrolysis, with the result that they are found to be in complete accord with the observations of the two last-mentioned chemists, thus rendering it probable that there will be found one fundamental law expressing the rate of change in all enzyme reactions which can be quantitatively studied with sufficient accuracy.

If we desire to follow the course of a starch transformation as a function of the time, there are two methods open to us, one based on the diminution of the optical activity of the solution, the other on the augmentation of the cupric reducing power of the mixed products of change.

It has been frequently shown by one of us (Brown and Millar, *Trans.*, 1899, 75, 315) that when soluble starch is transformed by an active diastase at temperatures below 60°, the hydrolysed solution speedily attains definite optical and reducing properties corresponding to a well-defined molecular decomposition of the original starch. This point is reached when the mixed products of hydrolysis have attained a specific rotatory power of  $[\alpha]_D 150^\circ$ , and a cupric reducing power of  $R\ 80$ ;  $R$  being expressed in terms of maltose per cent. of the mixed products. This stage of the reaction is so well defined and permanent that it may be regarded, under ordinary conditions of starch transformation, as an indication that hydrolysis is complete. If, therefore, we ascertain either the total fall in rotation (which may be expressed either in degrees or in arbitrary scale units), or the increase in cupric reduction which a given solution of starch experiences in attaining this final resting stage, then the rotation or reduction at any intermediate stage will give us a measure of the amount of hydrolysis at that particular moment of time.

We have employed both these methods during the investigation, but since it is impracticable to use solutions of soluble starch of greater concentration than from 3 to 4 per cent., the total fall in optical activity is not large, and the errors of reading of the polarimeter consequently assume a very sensible magnitude relative to the total fall. Under these conditions, the optical method is far less accurate as a measure of the progress of the reaction than that based on cupric reduction, which is the one which latterly was exclusively employed.

The experiments we have cited in this paper were carried out as follows.

A 3 per cent. solution of soluble starch, prepared by Lintner's acid method, was maintained at a constant temperature in a thermostat, and to a known volume of the solution was added a small, definite



amount of a cold water extract of an actively diastatic malt, the time of this addition being accurately noted. In those cases in which the transformation was to take place at an elevated temperature the malt extract was previously heated for an hour at that temperature, or a little above.\* The amount of malt extract was arranged with due regard to the temperature at which the transformation was to take place, and was so adjusted that the reaction did not progress too rapidly for the subsequent operations.

After the commencement of hydrolysis, and at carefully noted intervals, portions of the liquid amounting to exactly 25 c.c. were quickly taken out with a pipette, and were at once mixed with about double the volume of *boiling* water, the temperature of the mixture being sufficiently high to at once arrest further diastatic action. After boiling for a few minutes, the solution was evaporated and accurately made up to its original volume. The cupric reducing power was then determined gravimetrically with Fehling's solution under the standard conditions laid down in a previous paper (Brown, Morris, and Millar, *Trans.*, 1897, 71, 94). Meanwhile a portion of the original starch solution had been hydrolysed completely down to the final stage by digestion for an hour at 50° with a very active malt extract added at the rate of 5 c.c. or more per 100 c.c. of the solution. This, of course, gave the maximum reducing power of the fully hydrolysed starch, and the ratios of the intermediate reductions to this amount afforded a measure of the hydrolysis at each stage. It is scarcely necessary to add that all the necessary corrections were introduced for the reducing power and the volume of the malt extract employed, for the small initial reducing power of the soluble starch itself, and for the changes of volume of the abstracted samples due to temperature.

From the experimental data so obtained, the 'coefficient of velocity' was either directly calculated or, as was generally the case, the results were plotted out on a system of rectangular coordinates, representing on the one hand equal time intervals, and on the other the proportion of hydrolysable substance still left in solution. A perfectly even curve was then drawn through the experimental points with the aid of a flexible lath.

If we denote the cupric reduction of unit volume of a completely hydrolysed starch solution as *unity*, and take  $x$  as the ratio of the reduction observed at any given time reckoned from the commencement of the reaction, then, if the time curve representing the course of the hydrolysis is logarithmic,

$$\frac{1}{\theta} \log \frac{1}{1-x} = k,$$

\* This is a necessary precaution, in order to avoid any slow changes in the activity of the extract after it has been added to the hot solution of starch,

where  $k$  is a constant representing the 'coefficient of velocity' of the hydrolysis, and  $\theta$  is the time elapsed.

The results of a few typical examples of experiments of this kind are given in the Tables appended to the paper, the values of  $k$  deduced from the above formula being given in the fourth column.

Table I records a transformation carried out at a temperature of  $51-52^\circ$  for more than  $2\frac{1}{2}$  hours, during which time, as will be seen from the value of  $1-x$  at the close of the experiment, 95 per cent. of the full hydrolytic change had taken place.

It will be noted that throughout the reaction there is a steady augmentation in the value of  $k$ . This is an invariable feature of all our numerous experiments, and proves that the course of the hydrolysis does not conform to the above logarithmic expression.

If we assume that the normal curve expressing the rate of change is logarithmic, but that its form has been modified by secondary disturbing causes, then the constant augmentation of  $k$  points to a set of conditions which is producing a constant acceleration in the velocity of change. In other words, within any given time interval there is somewhat more of the residual substance hydrolysed than there should be according to the logarithmic formula.

In an early stage of the inquiry, when we still had reason to believe that this was an exceptional instance of departure from the "mass law," we were led by certain considerations to search for the disturbing cause in the complex intermediate products of hydrolysis. We certainly cannot account for the results by assuming that they are due to the gradual accumulation of the products of change, with a consequent tendency to chemical reversion, since any influence of this kind will tend to diminish, not to increase, the velocity coefficient  $k$ .

Whatever differences of opinion may still exist as to the exact nature of some of the intermediate products of starch transformation, it is quite certain that, in course of its hydrolysis with diastase, soluble starch, unlike cane sugar under the action of invertase or acids, does not at once split up into its final products, maltose and a well characterised dextrin. This stage is reached only through a series of intermediate substances of the amylo-dextrin and malto-dextrin class. Now it is quite conceivable, although it has never been proved, that these intermediate substances may show a differential resistance to hydrolysis. If the hydrolysis of the lower members of the series is more readily effected than that of the products which stand in closer genetic connection with starch itself, these differential properties of the intermediate products would almost certainly show themselves by some such augmentation of the velocity coefficient as we have observed.

We attempted to solve this question experimentally in the following manner.

Two solutions, A and B, were prepared, containing the same amount of hydrolysable starch products, as measured by the amount of cupric reduction which the solutions gave on complete hydrolysis with an active malt extract. Solution A, however, contained starch products which had been only very slightly hydrolysed, whereas B contained more highly converted products, that is to say, a much larger proportion of those intermediate substances which, on the above assumption, ought to undergo hydrolysis more rapidly. To equal volumes of these solutions were added exactly equal quantities of a cold water malt extract, and the course of each reaction was followed by the time method already described, care being of course taken to keep all the conditions exactly the same for the two solutions. The result certainly did *not* confirm the above hypothesis of the more ready hydrolysis of the lower members of the series.

It was this failure to discover any reasonable explanation of the augmenting value of  $k$  in starch transformations, and our consequent inability to bring our observations into line with the analogous hydrolysis of cane sugar, which caused us to delay publishing our results four or five years ago.

If we critically examine the results of the two starch transformations given in Tables I and II appended to this paper, we see that the time-curve expressing the rate of hydrolysis is approximately represented by a straight line until from 30 to 40 per cent. of the total hydrolysis is complete. This is well shown in the last columns of Tables I and II, where we have given the increased amount of cupric reduction for equal intervals of time. Within the limits mentioned above, the amount of hydrolysis is *approximately proportional to the time*.

That the amount of transformation is, up to a certain point, a linear function of the time, is also well shown in the following experiment, where the observations have been restricted to a transformation of only 15.5 per cent. of the total hydrolysable products:

*Transformation of a 3 per cent. soluble starch solution with 1 c.c. of malt extract per 100 c.c. Temperature 21°.*

Time in minutes.	$x$ . Amount transformed. Total hydrolysis = 1.	Amount which should have been transformed if hydrolysis is directly proportional to the time.
5	0.038	—
10	0.077	0.076
20	0.155	0.152

In this case, the linear expression is almost strictly correct, that is to say, up to a point at which 15.5 per cent. is hydrolysed, we have equal amounts of transformation in equal times.

We may go further than this, and ascertain the nature of the curve after the linear elements of it have been passed. For this purpose, we have taken the results given in Table I at the end of the paper, and have commenced from the stage of the hydrolysis which was reached in 40 minutes, when 0.4355 of the complete hydrolysis had been attained, that is to say, when 0.5645 of hydrolysable substance was left. Making this last value the new starting point, and taking it therefore as unity, we obtain the following results on recalculation :

Old time units, minutes.	New time units.	$k$ .
40	—	—
50	10	0.00842
60	20	0.00831
70	30	0.00821
80	40	0.00837
90	50	0.00818
100	60	0.00807
110	70	0.00822
120	80	0.00840
130	90	0.00855

The values of  $k$  no longer show the steady increase which they do if we take the commencement of the transformation as our starting point, and their approach to equality shows that this part of the curve is approximately *logarithmic*.

We are able therefore to analyse our time curves and divide them into two parts, an earlier one which is *linear*, and a later one which is approximately *logarithmic*, the change from one expression to the other not being abrupt, but gradual. In his paper on enzyme action, Adrian Brown (this vol., p. 373) has brought forward a striking number of facts showing that the time-curve representing the action of invertase on cane sugar is not logarithmic, as had been previously believed, but that the value of  $k$  steadily augments during the reaction, just as we have found it do in the case of starch transformations. He has also shown that with varying concentrations of sugar, all other conditions remaining the same, approximately equal masses of the sugar are hydrolysed in equal times, providing the comparisons are made at an early stage of the hydrolysis ; in other words, the inversion up to a certain point is a linear function of the time.

Still more recently, V. Henri (*Compt. rend.*, 1901, 133, 891) has also shown that the velocity of inversion of cane sugar with invertase

increases more rapidly than is expressed by the ordinary logarithmic formula of a unimolecular change.

He proposes the following empirical formula as more accurately representing the course of the reaction :

$$\frac{1}{\theta} \log \frac{1+x}{1-x} = 2k_1.$$

We have applied this formula to the results obtained in our experiments on starch hydrolysis by diastase, and find that the values of  $k_1$  so obtained are much more nearly constant than those of  $k$  derived from the original logarithmic expression, as will be seen on looking at the values of  $k_1$  given in the fifth column of the appended tables. From what has been said, however, about the composite nature of the time-curve, it is improbable that any single mathematical expression will be found which is strictly applicable to all parts of the curve.

It is now perfectly clear that as regards the general course of the reactions there is a close parallelism between starch hydrolysis with diastase and inversion of cane sugar by invertase, and that the observed changes in the velocity coefficient of starch hydrolysis are not necessarily conditioned by the exceptional nature of the intermediate products. Both reactions are linear in the early stages, and both are influenced by variations in the concentration of the hydrolyte. The influence of decreasing concentration is to cause a larger proportion of the remaining substance to be hydrolysed than would be expected from the application of the 'mass law' of a unimolecular change, provided always the time units are reckoned from the commencement of the reaction. In the case of starch transformations, the simple logarithmic formula is fairly well applicable in dilute solutions when from 30—40 per cent. of the hydrolysis is complete. The same will probably be found to hold good with regard to cane sugar inversion.

Henri's formula is equally well applicable to both reactions.

Adrian Brown (*loc. cit.*) explains the results which he obtained in his experiments with cane sugar by assuming that an appreciable time elapses between the molecular union of the sugar and enzyme and the actual hydrolysis, and that this time interval necessarily limits the amount of work which the enzyme can perform, so that when the ratio of sugar molecules to enzyme molecules is large, a certain maximum amount of hydrolytic work is accomplished by the latter which cannot be exceeded, and that no increased effect is consequently produced by increasing the concentration of the sugar, all other conditions remaining the same. He obtained apparent confirmation of this by gradually decreasing the concentration of the sugar, the enzyme remaining constant in amount. He then found, when a certain low point of concentration had been reached, that the reac-

tion approximately conformed to the mass law, that is, was independent of concentration.

It appears to us that the time-curves representing enzyme action can be explained in a somewhat different manner, and without postulating any differences in the time intervals between the successive stages of the reaction other than those due to variations in the respective masses of the reacting substances existing in unit volume.

It will simplify matters if we consider the case of the inversion of cane sugar, although the same argument, with a little modification, is equally applicable to the hydrolysis of starch.

When cane sugar is inverted with dilute *acids* of different kinds, but of the same *molecular concentration*, the velocity coefficients of hydrolysis not only vary in the same order as the electric conductivities of the dilute acids, but there is also a remarkable numerical agreement in the values representing the invertive action on the one hand, and the electric conductivity on the other.

The striking general agreement between these two properties has been emphasised by Ostwald, who has shown that it exists for a large number of acids (see "Outlines of General Chemistry," p. 360).

This can be explained by assuming that the velocity coefficient of inversion is a function of the number of molecules of electrolytically dissociated *ions* per unit volume of the solution.

The number of free hydrogen ions in unit volume of the most dilute acids which have hitherto been employed in such experiments must be very large compared with the number of cane sugar molecules, and under these conditions it might be expected that the course of the reaction would be expressed, as it actually is, by the logarithmic formula of a simple mass action, since for all practical purposes the cane sugar is the only substance of which the mass is changing. In the case of *enzyme* hydrolysis, such as that effected by invertase, the apparent active agent is a non-electrolyte, incapable of any appreciable dissociation, and at first sight it would appear that notwithstanding the identity of final products, there is some essential difference between acid and enzyme hydrolysis. We believe this is only apparent, and that enzyme hydrolysis is also brought about either by active water ions, or by active water molecules dissociated from the inactive and large aggregates of which the liquid mainly consists.

Pure water is in itself not a perfect non-electrolyte, but even if it were, we are never dealing with pure water in such experiments, and the remarkable influence of very minute but sensible amounts of acid in intensifying the action of invertase and diastase is so well established as in itself to suggest that water dissociation in some form or

other is intimately bound up with the action of these and other enzymes.\*

The ordinary conditions of feeble acidity necessary for the complete development of these enzyme actions are not sufficient to produce any appreciable direct hydrolytic action on the cane sugar within the time ordinarily occupied by such an experiment and within the limits of temperature necessarily imposed. In such cases, however, there can be little doubt that hydrolysis is preceded by a combination of the hydrolyte with the enzyme, and that this combination is much more unstable and less able to withstand the action of the active ions or dissociated molecules of the electrolyte than the original cane-sugar.†

According to this view these active ions are the true hydrolysts, not the enzyme itself, which has only an intermediate function, and it is now necessary to consider how this way of looking at the facts will affect our conception of the rate of change of the hydrolyte.

A solution of cane sugar undergoing hydrolysis by invertase must contain the following substances :

*A*—the unaltered cane sugar.

*a*—the cane sugar in combination with the enzyme.

*b*—the added enzyme, a portion of which, *b'*, is at any one moment in combination with *a*.

$(a + b')$ —the combination of cane sugar and enzyme.

*a*<sub>1</sub>—the products of hydrolysis of *a*.

*x*—the free water ions, or dissociated water molecules, which act as the true hydrolysts.

It is assumed that, owing to favourable conditions, the number of active ions, *x*, is very large indeed compared with that of the other reacting molecules, and further that there is no difference in the respective velocities of the other reactions except those conditioned by the varying masses of the reacting substances in unit volume.

If we wish to follow an inversion experimentally, it is always

\* On the question of the influences of mere traces of acid on the action of diastase and invertase, see Baranetzky, *Die Stärkeumbildenden Fermente in den Pflanzen*, Leipzig, 1878; O'Sullivan and Tompson, *Trans.*, 1890, 57, 855; Brown and Morris, *Trans.*, 1890, 57, 511; Fernbach, *Journ. Fed. Inst. Brewing*, 1896, 128.

The extreme sensitiveness of both diastase and invertase to minute quantities of alkali in the solution becomes easy to understand if the hydrolytic action is conditioned by the presence of electro-positive ions.

† There is a considerable amount of experimental evidence in favour of there being a real combination of hydrolyte and enzyme prior to hydrolysis. The recent work of Emil Fischer, showing that there is some sort of stereochemical relationship between hydrolyte and enzyme, seems to point to the possibility of the enzyme itself holding the combined hydrolyte with some definite orientation, which facilitates the action of the active water ions upon it. The enzyme may be regarded therefore as the *vice* which holds the sugar molecule in a position favourable for the splitting agent to act.

necessary to restrict its velocity, and in order to do this the concentration of  $b$ , the added enzyme, must be very small in relation to the initial concentration  $A$  of the cane sugar. In the earlier stages of the hydrolysis therefore,  $A$  in unit volume will be very large compared with  $(a+b')$ , the combination of cane-sugar and enzyme present at any moment. But  $(a+b')$  must strictly speaking be considered the starting point from which the hydrolysis commences, the true hydrolyte, in fact, and the velocity of the inversion will depend on the concentration of  $(a+b')$ . So long as the concentration of the unaltered cane sugar  $A$  remains very large compared with  $(a+b')$ , this latter will remain almost constant, and equal amounts of inversion will take place in equal times: the time 'curve' will in fact be *approximately a straight line*. When, however, the concentration of  $A$  is materially reduced and begins to approach that of  $(a+b')$  in the order of magnitude, then, by the ordinary laws of mass action,  $(a+b')$  will gradually get smaller, and the rate of inversion will more nearly approach the logarithmic expression.\*

This explanation accords very well with all the known facts, as will be seen from the following considerations.

We have seen from the results obtained by the hydrolysis of starch by diastase that the first part of the time reaction is represented by a straight line. This has also been found to be the case by Adrian Brown as regards the inversion of cane sugar by invertase; not only do the first portions of the curves approach very nearly to straight lines, but he also finds that, with equal concentration of invertase, considerable variations in the initial concentration of the sugar up to a certain stage of the reaction do not materially affect the absolute amount of sugar inverted in a given time. This we should expect from what has already been said: when a certain point is reached, any increase in  $A$  no longer sensibly influences the value of  $(a+b')$ , which is really the regulating factor of the reaction, and so long as these conditions exist we have equal amounts of hydrolysis in equal times.

Our hypothesis also affords an explanation of Kjeldahl's empirical "law of proportionality," which may, in fact, be deduced from it. Kjeldahl found that the relative diastatic power of two solutions is expressed by the cupric reducing power produced in a given time when the enzyme solutions act on the same weight of starch at the same temperature, provided always the reducing power is not allowed to go

\* We have here, for the sake of simplicity, omitted any reference to the disturbing influence produced by the accumulation of  $a_1$ , the products of inversion. Towards the close of a hydrolysis of a fairly concentrated solution this effect is unquestionably noticeable, but we doubt whether it has much influence in determining the form of the curve of dilute solutions, such as we used for starch transformations.



beyond  $R$  40—49.\* This corresponds to the hydrolysis of from 50 to 60 per cent. of the starch. It is clear, however, from an inspection of Kjeldahl's own curves, expressing the amount of hydrolysis with varying quantities of diastase, that the reaction is not by any means rectilinear as far as  $R$  40, although it may be sufficiently so for all practical purposes of diastasimetry. It is, however, very nearly straight as far as  $R$  29, at which point about 36 per cent. of the full hydrolysis is complete. This corresponds very closely with our own observations, already referred to, on the straight part of the curve.

The conditions of Kjeldahl's experiment amount to increasing the concentration of  $b$ , and consequently of  $(a + b')$ , leaving everything else the same. Under these circumstances, the hydrolysis effected in a given time will be approximately proportional to the concentration of  $(a + b')$ , provided the reaction is not allowed to go so far that the concentration of  $A$ , the untransformed hydrolyte, is no longer able to maintain the combination of the enzyme and hydrolysable substance practically constant. This is guarded against by making the comparisons for cupric reduction within the time during which the course of the reaction is practically rectilinear, and when, consequently, a large amount of hydrolysable material still remains.

We can also make another important deduction from our hypothesis, and predict that by largely increasing the relative amount of enzyme to hydrolyte, that is to say, increasing the value of  $(a + b')$  in relation to  $A$ , the more completely will the linear element of the time-curve be eliminated, and the more nearly will the course of the whole reaction

be represented by the unimolecular formula  $\frac{1}{\theta} \log \frac{1}{1-x} = k$ .

In actual practice, it is not possible to go very far in this direction, since the velocity of the action then becomes so great that the course of the hydrolysis cannot be followed with sufficient accuracy. The results of Adrian Brown's experiments on the inversion of very dilute solutions of cane sugar with fixed amounts of enzyme point, however, to the correctness of this deduction, for he found under these conditions that the "velocity-coefficient" was much less influenced by varying concentration; in other words, there was a much nearer approach, even in the earlier stages of the reaction, to the simple logarithmic expression of a unimolecular change.

We must express our thanks to Mr. D. McCandlish for assistance in the experimental part of this inquiry.

\* In his original paper (*Møddelselser f. Carlsberg Lab.*, 1, French *Résumé*, p. 117), Kjeldahl has employed an older form of notation for expressing the reducing powers. We have converted them into the usual form, which expresses the specific reducing powers in terms of percentage of apparent maltose.

In the following tables :

$\theta$  = the time units elapsed from the commencement of the experiment.

$x$  = the proportion of substance hydrolysed when 1 = total hydrolysable substance.

$k$  = "velocity-coefficient" from formula  $\frac{1}{\theta} \log \frac{1}{1-x} = k$ .

$k_1$  = velocity-coefficient from Henri's formula  $\frac{1}{\theta} \log \frac{1+x}{1-x} = 2k_1$ .

TABLE I.—Transformation of a 3 per cent. starch solution with 0.25 c.c. of malt-extract per 100 c.c. of solution. Temperature, 51–52°.

$\theta$ . Time in minutes.	$x$ .	$1-x$ .	$k$ .	$k_1$ .	Amount of trans- formation in equal time intervals.
10	0.1084	0.8916	0.00498	0.00472	
20	0.2250	0.7750	0.00553	0.00497	0.1166
30	0.3350	0.6650	0.00590	0.00504	0.1100
40	0.4355	0.5645	0.00620	0.00506	0.1005
50	0.5350	0.4650	0.00650	0.00518	0.0995
60	0.6150	0.3850	0.00690	0.00518	0.0800
70	0.6800	0.3200	0.00706	0.00514	0.0650
80	0.7385	0.2615	0.00728	0.00514	0.0585
90	0.7800	0.2200	0.00730	0.00504	0.0415
100	0.8150	0.1850	0.00732	0.00495	0.0350
110	0.8500	0.1500	0.00749	0.00495	0.0350
120	0.8800	0.1200	0.00762	0.00497	0.0300
130	0.9030	0.0970	0.00779	0.00497	0.0230
140	0.9220	0.0780	0.00791	0.00497	0.0190
150	0.9400	0.0600	0.00814	0.00503	0.0180
160	0.9500	0.0500	0.00813	0.00492	0.0100

TABLE II.—Transformation of a 3 per cent. starch solution with 1 c.c. of malt-extract per 100 c.c. of solution. Temperature, 21°.

$\theta$ . Time in minutes.	$x$ .	$1-x$ .	$k$ .	$k_1$ .	Amount of trans- formation in equal time intervals.
10	0.095	0.905	0.00433	0.00413	
20	0.191	0.809	0.00460	0.00419	0.096
30	0.285	0.715	0.00485	0.00424	0.094
40	0.378	0.622	0.00515	0.00431	0.093
50	0.465	0.535	0.00543	0.00437	0.087
60	0.543	0.452	0.00574	0.00445	0.083
70	0.623	0.372	0.00613	0.00457	0.080
80	0.703	0.292	0.00663	0.00479	0.080

TABLE III.—*Transformation of a 3 per cent. starch solution with 1 c.c. of malt-extract per 100 c.c. Temperature, 21°.*

$\theta$ . Time in minutes.	$x$ .	$1-x$ .	$k$ .	$k_1$ .
10	0.081	0.919	0.00366	0.00352
20	0.163	0.837	0.00386	0.00357
30	0.238	0.762	0.00393	0.00351
40	0.308	0.692	0.00399	0.00345
44	0.334	0.666	0.00410	0.00342
50	0.378	0.622	0.00412	0.00345
60	0.440	0.560	0.00419	0.00341
70	0.506	0.494	0.00437	0.00345

TABLE IV.—*Transformation of a 3 per cent. starch solution with 1 c.c. of malt-extract per 100 c.c. Temperature, 21°.*

$\theta$ . Time in minutes.	$x$ .	$1-x$ .	$k$ .	$k_1$ .
5	0.034	0.966	0.00298	0.00295
10	0.072	0.928	0.00323	0.00313
20	0.145	0.855	0.00339	0.00317
40	0.337	0.663	0.00446	0.00380
60	0.480	0.520	0.00473	0.00378
80	0.579	0.421	0.00469	0.00358
100	0.660	0.340	0.00468	0.00344
120	0.720	0.280	0.00460	0.00328
140	0.760	0.240	0.00442	0.00309

XXXVIII.—*The Union of Hydrogen and Oxygen.*

By H. BRERETON BAKER, M.A.

THE fact that a large number of chemical actions have been shown to be dependent on the presence of aqueous vapour has led to many experiments being made on the union of hydrogen and oxygen. Prof. H. B. Dixon and Prof. Victor Meyer found no apparent diminution in the velocity of this action when the gases were dried. I have myself obtained the same result in a number of experiments carried on during the last 10 years. Recently, however, a method for the preparation of very pure

hydrogen and oxygen was devised by Mr. F. R. L. Wilson and myself. Some years ago, Prof. Edward Morley pointed out the various impurities which were present in the gas produced in the electrolysis of sulphuric acid and potassium hydroxide solutions. Lord Rayleigh (*Proc. Roy. Soc.*, 1889, 45, 425), using the latter method, attempted to minimise the amount of hydrocarbon impurity derived from the presence of carbonate in the potassium hydroxide by the addition of a small quantity of barium hydroxide. Since, however, the action of barium hydroxide on potassium carbonate is a reversible one, and since the potassium hydroxide is present in large excess, the precaution was probably not a very effective one. The new method consists of the electrolysis of highly purified barium hydroxide. It has been shown that barium carbonate is insoluble in a solution of the hydroxide, and that hydrocarbons are absent from the hydrogen. At the same time, the oxygen is apparently quite free from ozone and hydrogen peroxide.

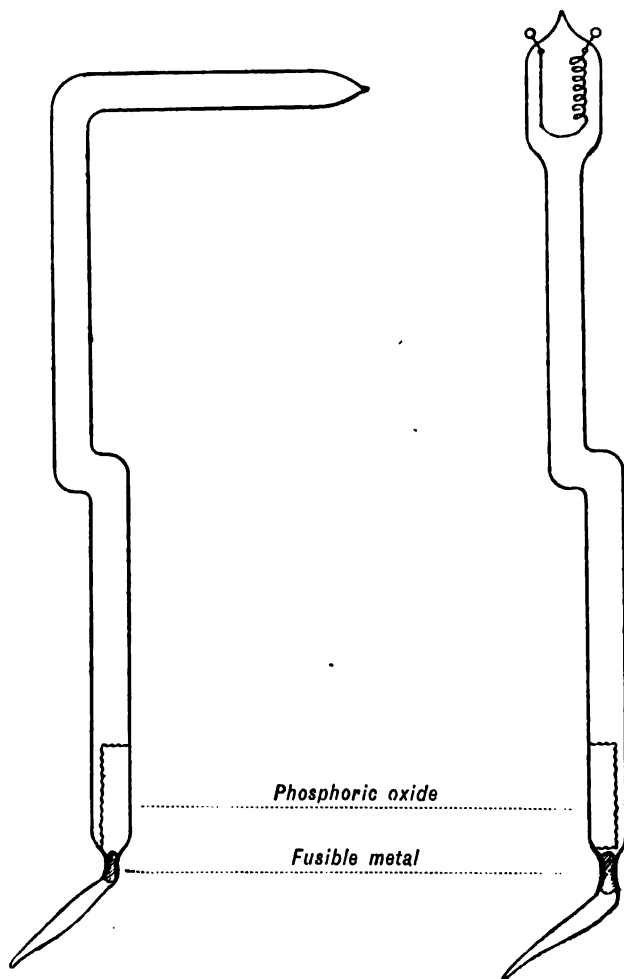
The use of this method suggested a new series of experiments on the union of hydrogen and oxygen, in which a new precaution has been found necessary. In a series of experiments, described later in the paper, it is shown that the undried hydrogen and oxygen combined very slowly in sunlight. It is, then, obviously necessary that the drying must take place in the dark, since the rate of the continued production of water in the light might conceivably be equal to the rate of its absorption by the drying agent.

In order to find if moisture had any effect on the combination of the dried gases, the following procedure was followed. It may be pointed out that the reaction is a very sensitive one, and the omission of any one of the precautions taken will almost certainly lead to the failure of the experiment. The glass used has been either hard Jena or hard Bohemian glass. Only one experiment has been made with soft glass; in it, combination took place at a low red heat. The tubes were bent into the shape indicated by Fig. 1 (p. 402). They were then filled with a mixture of nitric and chromic acids and boiled in the water-bath for 24 hours. After this cleansing, the tube was washed out with distilled water and fitted to the tapered end of the platinum tube of a condenser. Purified water was then distilled through the tube for an hour. After allowing it to drain, the tube was dried by heating it to redness, while a current of air, dried by distilled sulphuric acid, was drawn through it. A plug of distilled phosphoric oxide was introduced, the upper end of the tube drawn off, and the lower end drawn out to a capillary of about 0.5 mm. diameter. A small piece of fusible metal was introduced and the tube was exhausted. It was then connected with the electrolysis apparatus, the mixed gases being roughly dried by passing them through a phosphoric oxide tube a foot long. The barium hydroxide used had been recrystallised fifteen times; it was found not

to be radioactive. When the tube was full of gas, the fusible metal was melted and allowed to run into the capillary. When the wall of the capillary is thick there is no fear of the glass being cracked by the expansion of the metal. When the metal was cold, the outer portion of

FIG. 1.

FIG. 2.



the capillary was sealed in order to prevent any possibility of leakage round the metal. The tubes were then allowed to stand in the dark for varying periods. Comparative tubes were made at the same time from the same length of tubing and treated in precisely the same way, except that no phosphoric oxide was sealed up in them.

After 10 days' drying, two such tubes were heated side by side in the same Bunsen burner flame. In twelve experiments, the wet tube exploded and the dry tube did not. In only one experiment has a dry tube exploded, but in this case the tube had been carried for some miles by hand, and most probably some of the phosphoric oxide had been shaken into the part of the tube which was heated. In two experiments, where only 2 days' drying had been allowed, water was slowly formed in the dried tube, but although visible moisture was present, no explosive combination took place, and a slow combination only occurred. In each of the twelve experiments mentioned, the dried tubes were opened under mercury, a very small contraction was observed in some tubes, in most of them none at all. On addition of a small quantity of distilled water, the contents of each tube exploded on bringing them to a flame.

In order to see if increasing the temperature beyond the ordinary temperature of explosion ( $600^{\circ}$ , V. Meyer and Krause, *Annalen*, 1891, 264, 85) produced any effect, a thin coil of silver wire was attached to platinum wires by fusion, and the latter sealed through the walls of a hard glass tube (Fig. 2, p. 402). The tube was then dried as before and filled with the explosive mixture. It was found that no explosion took place, even when the silver was heated to its melting point by a current passed through it. No contraction was observed on opening the tube under mercury. The silver wire was drawn with great precaution from silver prepared for atomic weight purposes by the ammonium formate method.

Since a temperature of over  $1000^{\circ}$  was insufficient to bring about the union of the gases, a coil of thin platinum wire was substituted for the silver in the last experiments. The coil was cleaned *in situ* by nitric and chromic acids. It was heated by the current while the tube was being dried. After the admission of the explosive mixture, the tube was left attached to the mercury gauge for some hours. Even in its very imperfectly dried state, the gases seemed to be able to resist the catalytic action of the platinum. The tube was sealed as before, and left for ten days. At the end of this time there was no appearance of moisture on the surface of the phosphoric oxide. As this is a very delicate test for the presence of traces of water, it may be assumed that cold platinum wire has no effect on the dried mixture. The temperature of the platinum coil was raised by an electric current, and just after reaching visible redness the mixture exploded. The catalytic action of platinum is therefore apparently sufficient to bring about the union of the dried and purified gases at a low red heat.

Some twenty experiments have been made in order to find if electric sparks could be passed in the dried gas without explosion. In only one case has this been done, and only with extremely small sparks.

These sparks were accidentally obtained in a tube fitted with a silver coil, which, however, was not fused to the platinum wires, but only allowed to hang on them by its hooked ends. On passing a direct current through the coil, and shaking the tube at the same time, sparks were obtained at the points of contact of the two metals. No apparent combination resulted, although the process was repeated often in the course of the day. Next day the gases had become too dry to allow of the very small spark discharge passing through them. Other experiments in which sparks of less than 0.1 mm. from an induction coil were used, have, so far, always resulted in the explosion of the gases.

With regard to the explanation of the diminution of chemical activity in dried gases, it has always been asserted by Dr. Armstrong that, without an electrolyte, no chemical action is possible, and that the effect of removing water is only the removal of the possibility of an electrolyte being formed. This hypothesis is borne out in a very striking way by the behaviour of the partially dried gases. When they are heated, water is slowly formed, and although it is then present in enormously larger quantity than is necessary to bring about the action, no explosion takes place. It may be assumed that the water formed by the union of the very pure gases is itself very pure, and since pure water is not an electrolyte, then this water should not cause the explosion of the gases.

It has always seemed possible that this theory of Dr. Armstrong's should be pushed a step further by assuming that when water is present in the gases of ordinary purity, union can only take place by means of the ions produced by the dissociation of the gases. This extension of the ionic theory to moist gases seems to fit the experimental evidence fairly well, but it may be considered, *a priori*, that it is improbable that the very small quantity of water necessary [less than 3 mg. per 1,000,000 litres, according to Professor E. Morley's approximation (*Amer. J. Sci.*, 1889, 34, 200)] could act in the same way as liquid water. The fact, however, that feeble electric discharge cannot pass through dried gases lends support to this view.

I attempted to put the question to experimental trial by finding if any contraction in volume took place when a gas was dried from the point at which its moisture ceases to exert any measurable tension to the point at which the gas ceases to be chemically active. To effect this, a long tube shaped like a syphon barometer (Fig. 3) was carefully cleaned and dried as in the experiments described above. A sufficient quantity of mercury and a thin tube of distilled phosphoric oxide were introduced into the cylindrical bulb. The long tube was then exhausted, the mercury being boiled by playing on the surface of the tube with the flame of a Bunsen burner. The end of the barometer

tube was then sealed, the lower cylinder was then exhausted and filled with the gas, previously dried by a long phosphoric oxide tube. In the case of the explosive mixture, the side tube, opening under mercury, was made use of for introducing the gases, so that the mercury in the narrow tube served to disconnect the main bulb from the part of the tube which was heated in sealing. Six tubes were prepared in this way containing (1) hydrogen, (2) oxygen, (3) nitrogen, (4) air, (5) a mixture of hydrogen and oxygen; the sixth tube contained air without phosphoric oxide, and served for a standard. The tubes were rigidly fixed to a heavy iron stand on which they were wholly immersed in a deep tank with glass sides. A current of water was passed through the tank for two hours before the readings were taken, the water being obtained from a supply cistern. The readings were taken late at night, some 18 hours after the daily filling of the supply cistern. The apparatus was placed in a cellar without any outside walls, in which the temperature is remarkably constant. A thermometer reading directly to  $0.01^{\circ}$  was hung in the moving water. Readings were taken nightly for a month, the upper level of the mercury in the barometer tubes being read off by a cathetometer against a glass scale attached to the glass window of the tank. A difference of 0.1 mm. could be easily read, and by a simple calculation the difference of temperature is allowed for. Absolutely no difference was noted for the first month, and afterwards weekly readings were taken for six months, still with the same result. Hence a gas, on drying it to the utmost limit possible, does not change its volume by  $1/7000$ th, which is about the limit of error. This experiment does not, of course, prove that dissociation does not take place in moist or partially dried gas. It only shows that, if it does occur, it does not take place to the extent measured in the experiments. There is a point which is worthy of note, that dried hydrogen and oxygen do not combine to a measurable extent at the ordinary temperature in the dark.

In order to find if sunlight had any effect on the union of these gases, two tubes were prepared as in the last series of experiments. One contained the dried, and the other the undried, mixture of gases from the electrolysis of barium hydroxide. After reading, they were exposed outside a south window for four months, from September to

FIG. 3.





December. At the end of this time, readings were taken which showed no alteration in volume of the dried gas, whilst the undried mixture showed a contraction of one-twenty-third of its volume. Hence the precaution mentioned in the earlier part of the paper of drying the mixed gases in the dark was shown to be necessary.

### *General Conclusions.*

1. The gases produced by the electrolysis of purified barium hydroxide do not explode on heating to redness after drying with distilled phosphoric oxide.

2. The gases can be heated to the melting point of silver without combination.

3. If only partially dried, the gases unite slowly on heating, and although visible water is present, no explosion takes place.

4. The undried gases unite slowly in sunlight at the ordinary temperature, the dried gases do not.

5. There is no contraction observable during the thorough drying of gases, so that the dissociation of gases in the undried condition, if it exists, cannot be proved by volume measurements.

In conclusion, I wish to give my best thanks to Dr. Armstrong for much encouragement and advice which he has given me during the progress of the research.

DULWICH COLLEGE, S.E.

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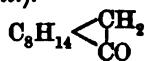
## XXXIX.—*Studies in the Camphane Series. Part VIII.* *m-Nitrobenzoylcamphor.*

By MARTIN ONSLOW FORSTER and FRANCES M. G. MICKLETHWAIT.

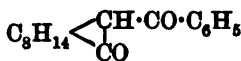
KETONES of the aliphatic series and of hydrogenised cyclic compounds have not been observed to form enolic modifications capable of separate existence. The tendency to change into a hydroxylic isomeride is first noticed when hydrogen, combined with a carbon atom adjacent to the carbonyl group, is replaced by an acyl radicle. During his investigation of 1:3-diketones, Claisen found that this disposition to undergo enolisation is influenced by the nature of the acyl substituent, becoming more pronounced as the negative character of that radicle increases (*Annalen*, 1896, 291, 37).

In view of this observation, we have prepared *m*-nitrobenzoylcamphor with the object of ascertaining whether that substance would

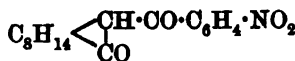
form, with benzoylcamphor and camphor itself, a series exhibiting the gradation of properties displayed by triacetylmethane, diacetylbenzoylmethane, acetyldibenzoylmethane, and tribenzoylmethane (*loc. cit.*).



Camphor.



Benzoylcamphor.

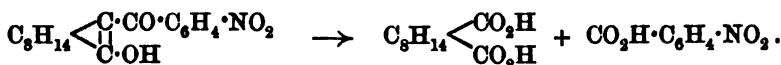


Nitrobenzoylcamphor.

On comparing benzoylcamphor with the nitro-derivative, it is found that the difference between them is almost as great as that subsisting between camphor and the benzoyl derivative. Camphor does not change into the enolic modification; benzoylcamphor, although stable in the solid form, rapidly changes into the isomeride when dissolved in chloroform, whilst *m*-nitrobenzoylcamphor shows so little disposition to undergo this transformation that it has not been found possible to obtain it in the ketonic form. That a small proportion of enolic *m*-nitrobenzoylcamphor becomes converted into the ketone is shown by a diminution in the specific rotatory power of a solution in chloroform; this amounts to less than 5 per cent. but until the neutral modification can be isolated it will not be possible to state the percentage of ketonisation represented by this change in optical activity.

Two methods suggested themselves for the preparation of a nitrobenzoylcamphor. In the first place, sodium camphor might be treated with nitrobenzoyl chloride, which would probably give rise to the nitrobenzoyl ester of enolic nitrobenzoylcamphor; this compound could be converted by hydrolysis into a nitrobenzoylcamphor, in which the nitro-group would occupy a known position. The alternative process consists in subjecting  $\alpha$ -benzoylbromocamphor to the action of nitric acid, the product, if a mononitro-derivative, being then reduced with alcoholic potash; the position of the nitro-group in the resulting nitrobenzoylcamphor could be ascertained by oxidation, which should give rise to one of the nitrobenzoic acids.

On consideration, the latter method appeared the more promising, and was therefore adopted. Each isomeric  $\alpha$ -benzoylbromocamphor, when treated with fuming nitric acid, yields a nitrobenzoylbromocamphor which, on reduction with alcoholic potash, is converted into enolic nitrobenzoylcamphor; potassium permanganate is immediately reduced by an alkaline solution of this compound, which is thus resolved into camphoric and *m*-nitrobenzoic acids.

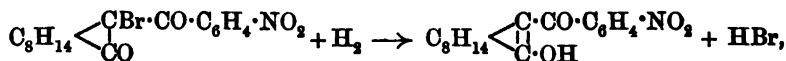


The *m*-nitrobenzoylbromocamphors described in this paper are related to one another in the same way as the benzoylbromocamphors from

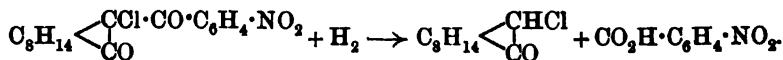
which they are derived. As already stated, the ketonic modification of *m*-nitrobenzoylcamphor has not been isolated, and consequently the influence on rotatory power exerted by the *m*-nitrobenzoyl radicle could not be compared directly with the effect produced when bromine is the substituent. We therefore refer to the derivative of lower melting point as  $\alpha$ -*m*-nitrobenzoyl- $\alpha$ -bromocamphor; this compound has  $[\alpha]_D + 87.9^\circ$  in chloroform and melts at  $93-94^\circ$ , whilst  $\alpha$ -*m*-nitrobenzoyl- $\alpha'$ -bromocamphor has  $[\alpha]_D - 26.1^\circ$ , and melts at  $101-102^\circ$ . If this nomenclature is uniform with that adopted in the case of the benzoylbromocamphors, it may be inferred that the optical influence of the *m*-nitrobenzoyl group is less powerful than that of the benzoyl radicle (compare Forster and Micklethwait, this vol., 163). The effect of the benzoyl radicle has been found to exceed that of a chlorine atom occupying the same position (*loc. cit.*), and is in turn exceeded by that of the bromine atom; it is probable that the optical influence of the *m*-nitrobenzoyl radicle is inferior to that of the chlorine atom, because  $\alpha'$ -*m*-nitrobenzoyl- $\alpha$ -chlorocamphor, which melts at  $72-74^\circ$ , has  $[\alpha]_D + 40.4^\circ$ , whilst the isomeride melting at  $110^\circ$  has  $[\alpha]_D + 7.1^\circ$ .

It will be noticed that in yielding a *m*-nitro-derivative, the  $\alpha\alpha$ -benzoylbromocamphors and  $\alpha\alpha$ -benzoylchlorocamphors conform to Crum Brown and Gibson's rule (*Trans.*, 1892, 61, 367), but although the *m*-nitro-compounds are produced almost exclusively, a small proportion of the *o*-nitro-derivative also is formed sometimes when the  $\alpha\alpha$ -benzoylbromocamphors are nitrated. We have been thus enabled to prepare enolic *o*-nitrobenzoylcamphor, identified by oxidation with potassium permanganate, which resolves it into camphoric and *o*-nitrobenzoic acids.

A comparison of the  $\alpha\alpha$ -nitrobenzoylbromocamphors with the corresponding chloro-derivatives has revealed one point of some interest. Whilst the first-named substances, on reduction with alcoholic potash, yield enolic *m*-nitrobenzoylcamphor and potassium bromide,



the  $\alpha\alpha$ -nitrobenzoylchlorocamphors, on similar treatment, are resolved into  $\alpha$ -chlorocamphor and potassium *m*-nitrobenzoate;



This affords an interesting example of the relative success with which derivatives of these two halogens resist the action of a reducing agent.

## EXPERIMENTAL.

*aa-m-Nitrobenzoylbromocamphor*,  $C_8H_{14} \begin{matrix} \swarrow CBr \cdot CO \cdot C_6H_4 \cdot NO_2 \\ \searrow CO \end{matrix}$ .

Owing to the readiness with which fuming hydrobromic acid converts  $\alpha'$ -benzoyl- $\alpha$ -bromocamphor into the isomeride, we were not prepared to find that the corresponding nitro-derivatives could be obtained by the direct action of fuming nitric acid, expecting that the unstable benzoyl-bromocamphor would yield the nitro-derivative of the stable isomeride. The earlier experiments were therefore conducted with a mixture of the two benzoylbromocamphors, but it was soon found that the product was not an individual substance, being resolved by fractional crystallisation into specimens of different specific rotatory power.

The two isomeric substances were therefore nitrated separately. Ten grams were covered with 30 c.c. of fuming nitric acid (sp. gr. 1.52), which dissolved the compound and became warm; after an interval of about 20 minutes, the liquid was poured into a large volume of cold water, the precipitated nitro-derivative being filtered, washed, and crystallised from methyl alcohol.

$\alpha'$ -m-Nitrobenzoyl- $\alpha$ -bromocamphor, prepared from  $\alpha'$ -benzoyl- $\alpha$ -bromocamphor and fuming nitric acid, separated in the form of a yellow, sticky mass on pouring the acid liquid into a large volume of water; it did not harden on continued washing or after an interval of several days. The substance was obtained in crystals by dissolving in the minimum quantity of hot methyl alcohol, allowing the liquid to cool, and decanting the clear solution from the yellow oil which separated; the deposit from this solution was recrystallised twice from hot methyl alcohol, from which it separates in long, flat, prismatic needles, pale yellow in colour, and melting at 93–94°:

0.2536 gave 0.4994  $CO_2$  and 0.1120  $H_2O$ .  $C = 53.70$ ;  $H = 4.95$ .

0.2382 „ 0.1179 AgBr.  $Br = 21.06$ .

$C_{17}H_{18}O_4NBr$  requires  $C = 53.66$ ;  $H = 4.78$ ;  $Br = 21.05$  per cent.

A solution containing 0.4906 gram dissolved in 25 c.c. of chloroform at 21° gave  $\alpha_D + 3^{\circ}27'$  in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D + 87.9^{\circ}$ .

An attempt was made to convert the substance into  $\alpha$ -m-nitrobenzoyl- $\alpha'$ -bromocamphor by the agency of hydrobromic acid (sp. gr. 1.83), but a specimen which was allowed to remain in contact with the agent during 24 hours underwent no change in specific rotatory power during this period.

$\alpha$ -m-Nitrobenzoyl- $\alpha'$ -bromocamphor separated as a hard, granular precipitate when the solution of  $\alpha$ -benzoyl- $\alpha'$ -bromocamphor in fuming

nitric acid was poured into a large volume of cold water; after being recrystallised twice from methyl alcohol, it was obtained in aggregates of small, pale yellow needles melting at 101—102°:

0.5036 gave 15.6 c.c. nitrogen at 17° and 757 mm.  $N = 3.45$ .

0.2288 „ 0.1124 AgBr.  $Br = 20.90$ .

$C_{17}H_{18}O_4NBr$  requires  $N = 3.68$ ;  $Br = 21.05$  per cent.

A solution containing 0.4624 gram dissolved in 25 c.c. of chloroform at 21° gave  $\alpha_D -58'$  in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D -26.1^\circ$ .



Twenty-seven grams of nitrobenzoylbromocamphor were dissolved in 150 c.c. of alcohol which had been distilled from caustic soda; the solution was then heated in a reflux apparatus with 8.5 grams of potassium hydroxide during  $1\frac{1}{2}$  hours, after which the alcohol was distilled off and the residue dissolved in about 100 c.c. of water. The clear, pale red solution was saturated with carbon dioxide, which precipitated a pale yellow solid, slightly sticky at first, but rapidly becoming hard. The product was washed several times with water and crystallised twice from hot alcohol:

0.3037 gave 11.7 c.c. nitrogen at 16° and 764 mm.  $N = 4.60$ .

$C_{17}H_{19}O_4N$  requires  $N = 4.65$  per cent.

The substance dissolves readily in alcohol, from which it crystallises in long, pink, silky needles which melt at 106—107°; it is insoluble in cold petroleum, and not very soluble in the warm liquid, from which it separates in rosettes of needles. Aqueous alkalis dissolve the compound, which is precipitated from the solution by carbon dioxide. Ferric chloride develops an intense purple coloration with alcoholic solutions, and a green precipitate is formed with copper acetate. A solution in chloroform immediately decolorises bromine, and potassium permanganate is reduced by cold solutions in alkali hydroxide.

*m*-Nitrobenzoylcamphor has not been obtained in the ketonic modification; a specimen was heated with boiling formic acid in a reflux apparatus during 2 hours and then precipitated by water, but the product dissolved readily in alkalis and developed an intense coloration with ferric chloride. The only evidence of a tendency to undergo transformation into the isomeride is the slight change exhibited by the specific rotatory power of a solution in chloroform during an interval of several hours.

0.4892 gram dissolved in 25 c.c. of chloroform at 20° gave  $\alpha_D 8.12'$  in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D +209.5^\circ$ ,

which in the course of several days diminished to  $[\alpha]_D + 200.1^\circ$ , remaining constant at that point.

The same slight reduction in specific rotatory power is immediately effected by adding a single drop of piperidine to the solution.

The *acetyl* derivative was prepared by heating the substance with acetic anhydride in a reflux apparatus during 2 hours; the liquid was then poured into a large volume of cold water, the viscous product being thoroughly washed with water and treated with a small quantity of cold alcohol:

0.2826 gave 10.3 c.c. nitrogen at  $14^\circ$  and 774 mm.  $N = 4.36$ .

$C_{19}H_{21}O_3N$  requires  $N = 4.08$  per cent.

The substance is readily soluble in alcohol, and is most conveniently crystallised from warm light petroleum, which deposits it in clusters of pale brown needles melting at  $127-128^\circ$ . The alcoholic solution is indifferent towards ferric chloride.

*Conversion into m-Nitrobenzoylbromocamphor.*—The unsaturated character of enolic benzoylcamphor is reproduced in the nitro-derivative, which is converted by bromine into *m*-nitrobenzoylbromocamphor. A solution of 3.6 grams of bromine in glacial acetic acid was added to 6.1 grams of the nitro-compound dissolved in glacial acetic acid containing 2.6 grams of dried sodium acetate in solution. The colour of the halogen was destroyed, and on pouring the liquid into a large volume of cold water a somewhat sticky precipitate was obtained; this was washed several times with water and crystallised from methyl alcohol, which deposited pale yellow needles melting at  $90-94^\circ$  and giving  $[\alpha]_D + 59.0^\circ$  in a 2 per cent. solution in chloroform. The product was therefore impure  $\alpha'$ -*m*-nitrobenzoyl- $\alpha$ -bromocamphor.

*Oxidation of m-Nitrobenzoylcamphor.*—An alkaline solution containing 3.5 grams of enolic *m*-nitrobenzoylcamphor was treated with 300 c.c. of a 2 per cent. solution of potassium permanganate, which was added in small quantities at a time to the cooled liquid. The deep green solution was warmed, and treated with alcohol until the manganate was completely reduced, the hydrated oxide being then filtered. The liquid having been evaporated to a small bulk and the crystallised potassium sulphate removed, dilute sulphuric acid was added until no further precipitation occurred. On dissolving the mixed acids in ammonia and adding lead acetate to the hot neutral solution, a bulky, white precipitate was formed; this was filtered and extracted with boiling water until the washings gave only a faint coloration with ammonium sulphide.

The precipitated lead salt was then treated with a boiling solution of sodium carbonate, filtered from lead carbonate, evaporated to small bulk, and acidified with dilute sulphuric acid. Camphoric acid was

thus obtained, and after being crystallised twice from boiling water, melted at 183—184°.

The filtrate from lead camphorate was united with the washings, evaporated to a small bulk, boiled with sodium carbonate, filtered, and acidified with dilute sulphuric acid, which precipitated *m*-nitrobenzoic acid (m. p. 141°).



On reducing with alcoholic potash a specimen of nitrobenzoylbromocamphor obtained from evaporated mother liquors, it was noticed that the pale yellow needles of enolic *m*-nitrobenzoylcamphor were associated with pale brown, transparent prisms; the same substance was occasionally produced in small and uncertain quantity from recrystallised nitrobenzoylbromocamphor. After recrystallisation from alcohol, it melted at 118°:

0.2524 gave 10.4 c.c. nitrogen at 18° and 771 mm.  $N = 4.82$ .

$C_{17}H_{19}O_4N$  requires  $N = 4.65$  per cent.

A solution containing 0.4647 gram in 25 c.c. of chloroform at 21° gave  $\alpha_D + 1.39'$  in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D + 44.5^\circ$ ; after an interval of three days, the same solution gave  $[\alpha]_D + 60.5^\circ$ , remaining constant.

At first it seemed probable that the substance just described was the ketonic modification of *m*-nitrobenzoylcamphor, but it was soon found that alcoholic solutions develop colour with ferric chloride and yield a precipitate with copper acetate; moreover, it dissolves in alkalis, and generally resembles enolic *m*-nitrobenzoylcamphor in chemical behaviour. It was ultimately identified as enolic *o*-nitrobenzoylcamphor by oxidising it with potassium permanganate under the conditions which convert *m*-nitrobenzoylcamphor into camphoric and *m*-nitrobenzoic acids. In this manner, camphoric acid was obtained in association with *o*-nitrobenzoic acid (m. p. 148°).



The benzoylchlorocamphors were dissolved in fuming nitric acid, the solution, after an interval, being poured into a large volume of cold water. As in the case of the corresponding bromo-derivatives, the product from the benzoylchlorocamphor of the higher melting point was much more granular in the crude state than the isomeride, which exhibits a tendency to remain sticky.

*α'-m-Nitrobenzoyl-α-chlorocamphor* crystallises from alcohol in aggregates of pale yellow prisms and melts at 72—74°:

0.2962 gave 11.3 c.c. nitrogen at 11° and 760 mm.  $N = 4.54$ .

0.2024 „ 0.0890 AgCl.  $Cl = 10.88$ .

$C_{17}H_{18}O_4NCl$  requires  $N = 4.17$ ;  $Cl = 10.58$  per cent.

A solution containing 0.5616 gram, dissolved in 25 c.c. of chloroform at 20°, gave  $\alpha_D + 1.49'$  in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D + 40.4^\circ$ .

*α-m-Nitrobenzoyl-α'-chlorocamphor* separates from alcohol in small, nearly colourless needles melting at 110°:

0.2533 gave 9.6 c.c. nitrogen at 13° and 755 mm.  $N = 4.44$ .

0.1824 „ 0.0770 AgCl.  $Cl = 10.44$ .

$C_{17}H_{18}O_4NCl$  requires  $N = 4.17$ ;  $Cl = 10.58$  per cent.

A solution containing 0.4379 gram dissolved in 25 c.c. of chloroform at 21° gave  $\alpha_D + 15'$  in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D + 7.1^\circ$ .

#### *Reduction of m-Nitrobenzoylchlorocamphor with Alcoholic Potash.*

Thirteen grams of *α'-m-nitrobenzoyl-α-chlorocamphor* were dissolved in alcohol and heated in a reflux apparatus with 4 grams of potassium hydroxide during  $1\frac{1}{2}$  hours; alcohol was then removed on the water-bath and the residue treated with water. Carbon dioxide was then passed through the liquid, and the precipitate, a portion of which had appeared on first adding water, filtered, washed, and crystallised twice from alcohol. It was then found to contain chlorine, but no nitrogen:

0.1958 gave 0.1527 AgCl.  $Cl = 19.29$ .

$C_{10}H_{18}OCl$  requires  $Cl = 19.11$  per cent.

The substance crystallised in thin, lustrous, white plates melting at 92°, and gave  $[\alpha]_D + 95^\circ$  in chloroform; it was thus identified as *α-chlorocamphor*.

The aqueous filtrate from chlorocamphor was acidified with hydrochloric acid, which precipitated *m-nitrobenzoic acid* melting at 139°.

#### *Reduction of the Benzoylchlorocamphors with Alcoholic Potash.*

The unexpected difference in the behaviour of the *m-nitrobenzoylchlorocamphors* and *m-nitrobenzoylbromocamphors* towards alcoholic potash led us to inquire whether the benzoylchlorocamphors are distinguished from the benzoylbromocamphors in the same respect. It has been already ascertained (this vol., 165) that the benzoylbromocamphors



yield enolic benzoylcamphor when reduced with alcoholic potash. On subjecting the benzoylchlorocamphors to this treatment we found that  $\alpha'$ -benzoyl- $\alpha$ -chlorocamphor yields enolic benzoylcamphor,  $\alpha$ -chlorocamphor, and benzoic acid, whilst the two last-named substances alone are produced when  $\alpha$ -benzoyl- $\alpha'$ -chlorocamphor is reduced.

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## XL.—*The Union of Hydrogen and Chlorine. Part IV. The Draper Effect.*

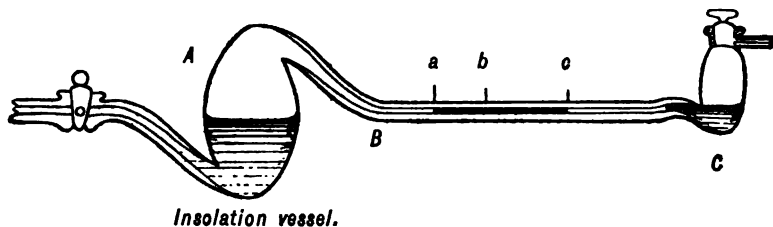
By J. W. MELLOR and W. R. ANDERSON.

IN 1843, Draper\* (*Phil. Mag.*, 1843, [iii], 23, 403, 415) published a very curious observation to the effect that if light from an electric spark is allowed to fall upon a mixture of equal volumes of hydrogen and chlorine gases, the volume of the mixture suddenly expands and immediately returns to its original condition. In the first part of this work, this phenomenon was called the *Draper effect*.

Pringsheim rediscovered the momentary expansion in 1887 and considered that it was in no way analogous to the Budde photo-expansion, since chlorine alone does not expand under the same conditions.

The Draper effect is best demonstrated in the following apparatus :

FIG. 1.



The mixed gases are contained in a flat glass bulb, *A*, called the insolation vessel. The lower part of the insolation vessel usually contains some water saturated with the two gases. The capillary tube, *BC*, contains a thread of liquid (*ac*) to serve as an index. Under the influence of a flash of light, the thread of liquid (*ac*) is pushed outwards to return immediately to its original position. Thus, *a* travels to *b* and immediately returns to *a*. Bunsen and Roscoe's method

\* After this, only historical references omitted in the earlier parts of this work will be given here.

is the best way of preparing the gases. The spark from an induction coil, intensified by means of a Leyden jar battery is the source of light, which may be from 10 to 20 cm. away from the insolation vessel.

In 1897, Wild and Harker (*Electrician*, 1897, 38, 690) found that sparks from a Wimshurst machine were as active as those derived from the coil, and that the magnitude of the effect varied directly as the visual brightness of the spark.

Although Hertz has shown that chlorine and most coloured gases and vapours partially absorb ultra-violet rays, Wild and Harker did not succeed in detecting any action which could be attributed to the presence of ultra-violet rays of light. The interposition of a layer of any substance, like glass or mica, opaque to the ultra-violet rays made no perceptible difference to the effect obtained. Wild and Harker hence conclude that the Draper effect is not due to the absorption of ultra-violet radiations by the gaseous mixture. Pringsheim's negative result with chlorine also confirms this conclusion.

Dixon and Baker (*Trans.*, 1896, 69, 1308; compare Rzewuski, *Wied. Beibl.*, 1896, 20, 1016; Hemptinne, *Zeit. physikal. Chem.*, 1896, 21, 493; J. J. Thomson, *Proc. Camb. Phil. Soc.*, 1901, 11, 90) have obtained negative results with Röntgen radiations. J. J. Thomson (*loc. cit.*) has found thorium radiations do not perceptibly influence the magnitude of the Draper effect. He also failed to detect any free ions in the gas under conditions which would have enabled him to observe one in  $10^{14}$  of the molecules present.

In addition to these isolated observations, we have observed the following facts:

*Influence of Variation in the Composition of the Illuminated Gas.*

We have been unable to detect the Draper effect when light is flashed upon:

1. Chlorine gas under pressures varying from one to half an atmosphere:
2. Chlorine gas at atmospheric or half the atmospheric pressure and heated from  $15^{\circ}$  to  $100^{\circ}$ :
3. Dry chlorine, or chlorine saturated with steam:\*
4. When chlorine is mixed with half its volume of nitrogen, air, carbon dioxide, carbon monoxide,† or methane.‡

\* One of us has shown that hydrogen chloride is formed when a mixture of chlorine and water vapour is strongly illuminated by an arc light.

† We once obtained a slight indication, but were never able to repeat it.

‡ Nothing very definite appears to have been published on the behaviour of mixtures of methane and chlorine in sunlight. Gay Lussac and Thenard record that a mixture of 2 vols. of methane and 4 vols. of chlorine deposit carbon and form 8 vols. of hydrogen chloride in daylight. Dumas says a mixture of 2 vols. of methane and 6 vols. of chlorine will explode in diffuse daylight.

5. Moreover, Professor Dixon (private communication) has failed to obtain the Draper effect with a dry mixture of hydrogen and chlorine gases, using concentrated sulphuric acid for the index fluid.

When chlorine is mixed with an equal volume of hydrogen confined over water saturated with the two gases, the Draper effect is readily obtained, but not if the proportions of the compounds differ by more than 3 per cent. from equality. The best results are given by the "sensitive mixture" of Bunsen and Roscoe.

It has also been observed that this mixture detonates most readily when exposed to a magnesium light.

### *The Action of Different Sources of Light.*

We have enclosed a magnesium lamp in a box fitted with a Thornton-Pickard time shutter, and tried the effect of a momentary exposure of the mixture of hydrogen and chlorine gases to the magnesium light. The shutter must be set to give an exposure from one-sixteenth to one second duration. In this way, we have obtained better results than with the Ruhmkorff coil ( $1\frac{1}{4}$  in. spark) and Leyden jar (one quart capacity). With commercial ribbon burning at the rate of 2 cm. per second, we have obtained displacements of the index up to 12 cm., whilst with a spark we have never had a greater displacement than 2 cm. One of us manipulated the time shutter while the other observed the index motion through a cathetometer.

The Draper effect has not been obtained by ultra-red or by ultra-violet rays.

The experiments with the magnesium light show that the effect is not due to an electrical disturbance induced in the gas by the electrical discharge. A coating of lampblack on the glass is sufficient to prevent any sign of the Draper effect with either magnesium light or an electric spark.

The more readily the gases detonate under the influence of light, the greater the Draper effect. If the hydrogen and chlorine gases are [not in suitable proportions to produce an explosion under the influence of magnesium light, the Draper effect *may* sometimes be obtained with magnesium light and not with the electric spark.

If certain non-explosive mixtures of hydrogen and chlorine are exposed to magnesium light for two or three seconds, the index at *a* (Fig. 1, p. 415) will immediately expand and then contract faster than the eye can follow, right into the insolation vessel, owing to the formation of hydrogen chloride at nearly an explosive rate.

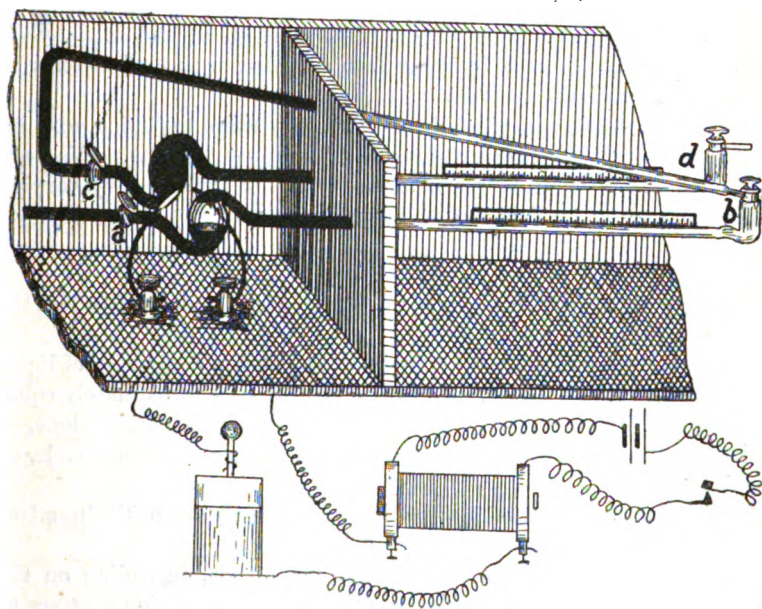
When a large expansion is taking place, the index moves in a series of rapid jerks, each about a centimetre in length. This appears to be due to friction between the index fluid and the walls of the capillary tube,

*Does Chemical Action take Place during the Draper Effect?*

It has hitherto been assumed that no hydrogen chloride is formed during the Draper effect because the index, after expansion, returns to its original position. If hydrogen chloride were formed, it is believed that the index would indicate a contraction in the volume of the mixed gases owing to the removal of hydrogen chloride by the water contained in the insolation vessel. We have tried to prove this in the following manner.

Two Bunsen and Roscoe's actinometers were filled with the same mixture of hydrogen and chlorine by leading the electrolytic gases into

FIG. 2.



the apparatus shown in Fig. 2, through the cock *a* and escape at *d*. The whole was enclosed in a box so that the index of each actinometer was screened from the rest of the apparatus by means of a dividing partition. All the glass parts on the left side of the partition were painted dead black with the exception of one-half of the bulb of one actinometer as shown in the figure. After the whole had been filled with a sensitive mixture of hydrogen and chlorine gases, the four cocks were closed. Temperature, pressure, and index readings were taken. The lid screwed on to the box and the whole was perfectly

screened from extraneous light. The electrical connections were made so that sparks passed midway between the insolation vessels of the two actinometers. A clockwork arrangement was fixed so that a spark passed between the terminals every half-hour.

One hundred and eight sparks gave a contraction of 3 cm., equivalent to about 2 per cent. contraction. In another experiment, 120 sparks at intervals of one hour caused a similar contraction. The darkened actinometer gave no indication of change.

It is necessary to allow some minutes to elapse between each spark, because Pringsheim has shown that if the sparks succeed each other after short intervals of time, the mixture will be carried through the period of induction when combination ensues.

The result of a number of similar experiments is to show that 100 sparks will cause a contraction up to about 2 per cent., indicating that hydrogen chloride is formed during the Draper effect, but in quantities too small to be detected by other than cumulative methods even with extra large insolation vessels.

The Draper effect may be likened to a very small explosion with insufficient energy to propagate itself throughout the gas. We have obtained effects of all magnitudes up to actual explosion, by varying the intensity of the light and the time of exposure.

#### *Conclusions.*

1. Hydrogen chloride is produced during the phenomenon called the Draper effect.
2. The Draper effect is only produced by the luminous rays of light.
3. The Draper effect occurs with mixtures of approximately equal volumes of hydrogen and chlorine, but not with chlorine alone, or mixed with steam, air, nitrogen, carbon dioxide, carbon monoxide, or methane.
4. The amount of combination depends not only upon the number, but also upon the intensity of the sparks.
5. When the effect reaches a certain magnitude, depending on the "sensitivity" of the gas, explosion occurs. An explosion appears to be a large Draper effect.
6. The motion of the index fluid which occurs when the insolation vessel of Bunsen and Roscoe's actinometer is exposed to a flash of light appears to be brought about by some disturbance in the gas attending chemical combination.\*

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\* Malard and Le Chatelier have observed a "période du mouvement vibratoire" (not quite similar to the one under discussion) antecedent to the explosion of certain gaseous mixtures. See Dixon's Bakerian Lecture, *Phil. Trans.*, 1893, A, 184, 97.

## XLI.—Condensation of Phenols with Esters of Unsaturated Acids. Part VII.

By SIEGFRIED RUHEMANN.

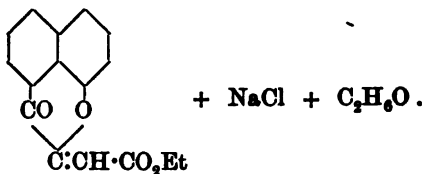
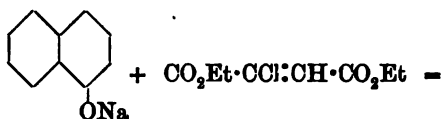
BENZO-1:4-PYRONE (chromone) and its homologues, as shown in this paper, have basic properties; they dissolve in hydrochloric acid, and these solutions give precipitates with cobalticyanic acid (Baeyer and Villiger, *Ber.*, 1901, **34**, 2679), as well as with platinic chloride. The hydrochlorides and the platinichlorides are, however, much less stable than the corresponding salts of dimethyl- $\gamma$ -pyrone, which can be recrystallised from water (Collie and Tickle, *Trans.*, 1899, **75**, 710).

Previously, only the monohydric phenols have been used for the formation of chromone and its homologues; since then, however, experiments have been made with the view of obtaining hydroxybenzopyrones from polyhydric phenols, but as these have been unsuccessful, I have attempted to prepare those compounds from the mono-ethers of the polyhydric phenols. One of these ethers, namely, guaiacol, had some time ago (Ruhemann and Stapleton, *Trans.*, 1900, **77**, 1180) been subjected to the action of ethyl phenylpropiolate, and the product which was thus formed had been found to suffer a decomposition analogous to that of the other aryl ethers of  $\beta$ -hydroxycinnamic acid. Guaiacol, as stated in this paper, reacts with ethyl chlorofumarate and forms ethyl guaiacoloxymumarate, which, on treatment with potash, yields the corresponding acid. Its transformation into methoxybenzo-1:4-pyrone and the subsequent hydrolysis of the methyl ether have not yet been carried out, as the study of the action of ethyl chlorofumarate on the naphthols has lately occupied my whole attention.

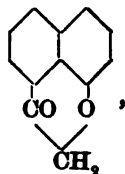
Whilst the ethyl ester behaves towards  $\beta$ -naphthol in the same manner as towards other phenols, and yields  $\beta$ -naphthoxymumaric ester, it reacts with  $\alpha$ -naphthol partly to form ethyl  $\alpha$ -naphthoxymumarate in the normal way, but chiefly to form two substances, one of which is an ester of the formula  $C_{16}H_{12}O_4$ , the other a compound of the composition  $C_{24}H_{12}O_4$ .

The facts, on the one hand, that this reaction is accompanied by the loss of alcohol, and, on the other, that the compounds have properties unlike those of the chromones, lead to the following view as to the formation and the constitution of the ester  $C_{16}H_{12}O_4$ :

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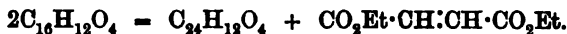


This compound may be derived from the tricyclic type,

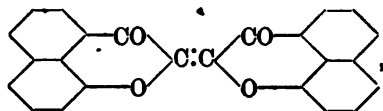


which I call naphtharone, and, accordingly, may be termed *ethyl naphtharonylacetate*.

The second substance,  $\text{C}_{24}\text{H}_{12}\text{O}_4$ , is perhaps formed from the first, according to the equation



The isolation of ethyl fumarate, figuring above, has not been effected as yet, but experiments to accomplish this task are in progress. The compound  $\text{C}_{24}\text{H}_{12}\text{O}_4$ , is, most probably, to be represented by the symbol



and may be called *bisnaphtharonyl*.

#### EXPERIMENTAL.

##### *Formation of Salts from Benzo-1:4-pyrone and its Homologues.*

The members of the chromone group dissolve in concentrated hydrochloric acid either in the cold or on slightly warming, and form salts which, however, are unstable, since the benzo-1:4-pyrone are precipitated on adding water, and are extracted by ether from their solutions in the acid. Cobalticyanic acid gives white, crystalline precipitates with solutions of the chromones in hydrochloric acid, and platonic chloride, dissolved in concentrated hydrochloric acid, yields platini-chlorides which separate in yellowish needles. These, however, are readily decomposed by water with the re-formation of benzopyrones.

The platinichlorides of chromone and some of its homologues have been analysed; for this purpose, they were washed with concentrated hydrochloric acid and dried in a vacuum over sulphuric acid and soda-lime. Owing to the unstable nature of those salts, the analytical numbers differ somewhat from those required by theory, as is shown in the following table:

Platinichlorides of—

Benzo-1 : 4-pyrone :

0.2605 left on ignition 0.0710 Pt. Pt = 27.21.

$(C_9H_6O_2)_2, H_2PtCl_6$  requires Pt = 27.71 per cent.

o-Toluo-1 : 4-pyrone :

0.2690 gave 0.0715 Pt. Pt = 26.58.

$(C_{10}H_8O_2)_2, H_2PtCl_6$  requires Pt = 26.65 per cent.

p-Toluo-1 : 4-pyrone :

0.2835 gave 0.0725 Pt. Pt = 26.58.

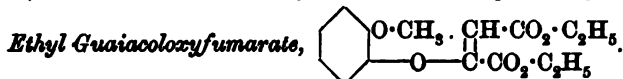
$(C_{10}H_8O_2)_2, H_2PtCl_6$  requires Pt = 26.65 per cent.

6 : 8-Dimethylbenzo-1 : 4-pyrone :

0.2937 gave 0.0732 Pt. Pt = 24.92.

$(C_{11}H_{10}O_2)_2, H_2PtCl_6$  requires Pt = 25.67 per cent.

*Action of the Sodium Derivative of Guaiacol on Ethyl Chlorofumarate.*



This compound is formed by adding ethyl chlorofumarate (1 mol.) to the hot solution of sodium (1 at.) in an excess of guaiacol. The dark, viscous product, when cold, is agitated with dilute sulphuric acid and ether; the ethereal layer is then freed from the excess of guaiacol by potash, the ether evaporated, and the remaining oil distilled in a vacuum. It has a yellow colour and boils at 212—213° under 15 mm. pressure. On analysis:

0.1925 gave 0.4333  $CO_2$  and 0.1075  $H_2O$ . C = 61.38; H = 6.20.

$C_{15}H_{18}O_6$  requires C = 61.22; H = 6.12 per cent.

*Guaiacoloxymumaric Acid*,  $(CH_3 \cdot O)^{[1]} \cdot C_6H_4 \cdot O \cdot C(CO_2H) : CH \cdot CO_2H$ .—The potassium salt of the acid separates on boiling the ethyl ester with alcoholic potash for 2 hours. After evaporation of the alcohol, the residue is dissolved in water and the solution treated with an excess of dilute sulphuric acid, when an oil is precipitated consisting of the organic acid and guaiacol. The latter compound, which is



formed along with guaiacoloxyfumaric acid on hydrolysis of the ester, is removed by shaking the ethereal solution of the oil with sodium carbonate, adding dilute sulphuric acid to the aqueous layer, and extracting the organic acid about sixteen times with fresh quantities of ether. On distilling off the ether, a solid is left behind; this readily dissolves in boiling water and on cooling crystallises in yellowish needles, which melt at  $138^{\circ}$  with evolution of gas. On analysis :

0.2028 gave 0.4115  $\text{CO}_2$  and 0.0803  $\text{H}_2\text{O}$ .  $\text{C} = 55.34$  ;  $\text{H} = 4.39$ .

$\text{C}_{11}\text{H}_{10}\text{O}_6$  requires  $\text{C} = 55.46$  ;  $\text{H} = 4.20$  per cent.

Guaiacoloxyfumaric acid readily dissolves in concentrated sulphuric acid, forming a yellowish solution which, after standing for 24 hours, is poured into cold water. As no solid separates, the solution is extracted with ether, and on evaporation of the latter, a yellowish solid remains behind; this crystallises from hot water in slightly coloured needles which melt and decompose at  $251^{\circ}$ . This substance, which has not yet been further examined, is probably *o*-methoxybenzo-1:4-pyrone-carboxylic acid.



For the preparation of this compound, a method has been used similar to that which served for the formation of ethyl  $\alpha$ -naphtho-cinnamate (Ruhemann and Beddow, *Trans.*, 1900, 77, 989).  $\beta$ -Naphthol (1 mol.) is added to a solution of sodium (1 at.) in absolute alcohol, the alcohol is removed by heating the solution in a vacuum, first at  $100^{\circ}$  and finally at  $180-190^{\circ}$ ; ethyl chlorofumarate (1 mol.), dissolved in toluene, is then added to the dry naphtholate, when a dark brown solution is produced with development of heat. This is boiled in a flask, attached to a reflux condenser for 1 hour in order to complete the reaction, and, when cold, is agitated with dilute sulphuric acid and ether. The ethereal layer is freed from unchanged  $\beta$ -naphthol by shaking with potash, and, on evaporation of the ether and toluene, yields a dark oil which is fractionated under diminished pressure. Almost the whole quantity distils at  $240-242^{\circ}$  under 12 mm. pressure as a very viscous, fluorescent yellow oil. On analysis :

0.2145 gave 0.5398  $\text{CO}_2$  and 0.1130  $\text{H}_2\text{O}$ .  $\text{C} = 68.63$  ;  $\text{H} = 5.85$ .

$\text{C}_{18}\text{H}_{18}\text{O}_6$  requires  $\text{C} = 68.79$  ;  $\text{H} = 5.73$  per cent.

*$\beta$ -Naphthoxyfumaric acid*,  $\text{C}_{10}\text{H}_7\text{O}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , is obtained on hydrolysis of the ethyl ester by means of alcoholic potash. On mixing the reagents, a red coloration is produced, and, after a short time, the potassium salt of the acid is precipitated as a yellowish solid.

After boiling on the water-bath for 1 hour, the alcohol is distilled off, the residue dissolved in water, and the organic acid liberated by hydrochloric acid. For the removal of  $\beta$ -naphthol, which is formed along with  $\beta$ -naphthoxyfumaric acid, the precipitate is dissolved in sodium carbonate, the solution filtered and mixed with an excess of hydrochloric acid.  $\beta$ -Naphthoxyfumaric acid is insoluble in water, it dissolves with difficulty in ether, readily, however, in hot alcohol; but on boiling the solution for some time, decomposition takes place with liberation of  $\beta$ -naphthol. The acid crystallises in small, yellowish plates, which darken at about  $230^\circ$  and melt at  $236^\circ$  with evolution of gas. On analysis:

0.1773 gave 0.4223  $\text{CO}_2$  and 0.0613  $\text{H}_2\text{O}$ .  $\text{C} = 64.96$ ;  $\text{H} = 3.84$ .

$\text{C}_{14}\text{H}_{10}\text{O}_6$  requires  $\text{C} = 65.11$ ;  $\text{H} = 3.87$  per cent.

I am at present engaged in the study of the action of concentrated sulphuric acid on  $\beta$ -naphthoxyfumaric acid with the view of condensing it to  $\beta$ -naphtha-1:4-pyronecarboxylic acid, and hope to publish the result shortly.

#### *Action of Ethyl Chlorofumarate on $\alpha$ -Naphthol.*

This reaction is of especial interest since, as mentioned in the introduction,  $\alpha$ -naphthol differs from the other phenols in its behaviour towards the ethyl ester, inasmuch as it yields two substances which belong to a new class of cyclic compounds. The reaction is carried out in a manner similar to that employed in the preparation of ethyl  $\beta$ -naphthoxyfumarate; namely, by adding  $\alpha$ -naphthol (1 mol.) to an alcoholic solution of sodium (1 at.), removing the alcohol by distillation in a vacuum, finally at  $190^\circ$ , and mixing the dry naphtholate with ethyl chlorofumarate (1 mol.) dissolved in toluene. The action takes place with development of heat and is completed by boiling in a flask attached to a reflux condenser for 1—2 hours. The contents of the vessel consist of a yellowish, crystalline substance and a brown liquid; these are agitated with dilute sulphuric acid, and the crystals are collected and washed with ether. The solid represents the bisnaphtharonyl,  $\text{C}_{24}\text{H}_{12}\text{O}_4$ , referred to in the introduction, whilst the dark filtrate contains ethyl naphtharonylacetate,  $\text{C}_{16}\text{H}_{12}\text{O}_4$ , and ethyl  $\alpha$ -naphthoxyfumarate.

*Bisnaphtharonyl* is almost insoluble in all the ordinary solvents, hot alcohol only dissolving traces and yielding a yellowish, fluorescent solution. It dissolves readily, however, in boiling nitrobenzene, forming a dark red solution with a deep green fluorescence, from which, on cooling, it separates in orange needles. These are freed from the adhering solvent by washing with hot alcohol; they do not melt at  $335^\circ$ . On analysis:

0.1787 gave 0.5171  $\text{CO}_2$  and 0.0548  $\text{H}_2\text{O}$ .  $\text{C} = 78.92$ ;  $\text{H} = 3.40$ .

0.1760 „ 0.5100  $\text{CO}_2$  „ 0.0525  $\text{H}_2\text{O}$ .  $\text{C} = 79.02$ ;  $\text{H} = 3.31$ .

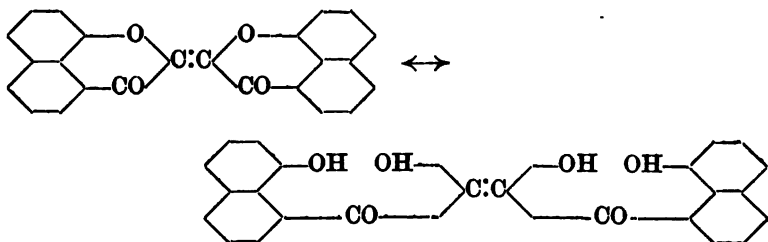
$\text{C}_{24}\text{H}_{12}\text{O}_4$  requires  $\text{C} = 79.11$ ;  $\text{H} = 3.30$  per cent.

Bisnaphtharonyl is insoluble in cold alkali, but dissolves when boiled with concentrated aqueous potash for 2 hours in a flask provided with a reflux condenser, forming a red solution. On adding hydrochloric acid, a yellowish solid is precipitated, which is insoluble in alcohol or acetic acid, but dissolves in nitrobenzene. From this solution, orange needles separate, which are no longer dissolved by cold potash. The properties of this compound point to its identity with bisnaphtharonyl, and this conclusion is supported by the following analysis:

0.1863 gave 0.5391  $\text{CO}_2$  and 0.0590  $\text{H}_2\text{O}$ .  $\text{C} = 78.91$ ;  $\text{H} = 3.51$ .

$\text{C}_{24}\text{H}_{12}\text{O}_4$  requires  $\text{C} = 79.11$ ;  $\text{H} = 3.30$  per cent.

This experiment proves that one or both rings, containing oxygen, in bisnaphtharonyl, open up by the action of potassium hydroxide, but under the influence of an acid close again to form the original compound. This may be symbolised as follows:



In the hope of effecting a deep-seated decomposition of bisnaphtharonyl which would supply further evidence for its constitution, I have subjected the compound to the action of fused potash, but found that complete carbonisation takes place.

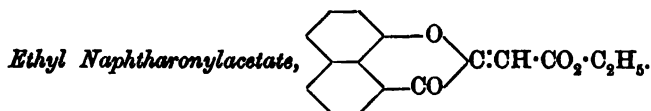
On adding concentrated sulphuric acid to the substance, it becomes purple and then dissolves very slowly at the ordinary temperature, but rapidly on slightly warming, to yield a red solution. This, when poured into water, gives a yellowish solid which is soluble in water with great ease. Most probably there is thus formed a sulphonic acid of bisnaphtharonyl; this view seems to be supported by the behaviour of nitric acid towards bisnaphtharonyl.

*Tetranitrobisnaphtharonyl*,  $\text{C}_{24}\text{H}_8(\text{NO}_2)_4\text{O}_4$ .—Bisnaphtharonyl dissolves in fuming nitric acid on warming slightly, and the red solution gives, with water, a yellowish solid. This is insoluble in the ordinary solvents, but dissolves in hot nitrobenzene, and on cooling crystallises in minute, yellowish-brown prisms, which are freed from the adhering

solvent by washing with hot alcohol. The compound does not melt at  $325^{\circ}$ . On analysis :

0.2590 gave 22.8 c.c. moist nitrogen at  $19^{\circ}$  and 778 mm.  $N = 10.36$ .

$C_{24}H_{18}O_{12}N_4$  requires  $N = 10.29$  per cent.

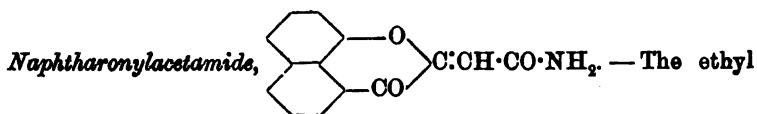


The dark mother liquor from bisnaphtharonyl, after being diluted with ether, is agitated with an excess of potash in order to free it from unchanged  $\alpha$ -naphthol. The ethereal layer, which has a deep green fluorescence, is then dried with calcium chloride, the ether evaporated, and the last traces of toluene removed by heating in a vacuum on the water-bath. The dark oil which remains behind, partly solidifies on standing. This product is dissolved in hot alcohol, and the solution, on cooling, deposits long, yellowish needles which after recrystallisation from the same solvent, melt at  $146-147^{\circ}$ . The substance is ethyl naphtharonylacetate. On analysis :

0.1992 gave 0.5225  $CO_2$  and 0.0805  $H_2O$ .  $C = 71.54$ ;  $H = 4.49$ .

$C_{16}H_{12}O_4$  requires  $C = 71.64$ ;  $H = 4.48$  per cent.

Ethyl naphtharonylacetate may be distilled in a vacuum, when it passes over as a yellowish oil which quickly solidifies; it is sparingly soluble in cold alcohol or acetic acid, but readily so on boiling. The hydrolysis of the ethyl ester is still under examination, but the results of a few experiments undertaken in that direction may be recorded here. On using alcoholic potash, a deep purple coloration of the solution takes place, and the alkaline liquor, after removal of the alcohol by distillation and solution of the residue in water, yields a brown, gelatinous precipitate on treatment with hydrochloric acid. This is insoluble in water, but dissolves in alcohol with the greatest ease and separates from the solution in an amorphous state. If aqueous, instead of alcoholic, potash is used for the hydrolysis, the ethyl ester dissolves on boiling for 2 hours. On adding hydrochloric acid to the reddish solution, a yellow precipitate is formed; this is a mixture of two or more acids which have not yet been separated.

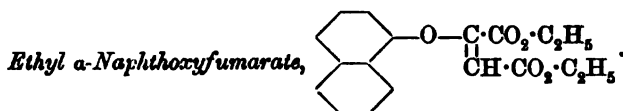


ester reacts with alcoholic ammonia on remaining in contact with it at the ordinary temperature for some time. The needles of

the ester gradually disappear, being transformed into a yellowish, crystalline product, whilst the solution turns pink. After 2 days, the precipitate is collected, washed with water, and then with alcohol. It is insoluble in either of these solvents, but dissolves in glacial acetic acid and crystallises from this solution in groups of yellowish needles which blacken at  $258^{\circ}$  and melt to a dark liquid at  $265^{\circ}$ . On analysis:

0.2395 gave 12 c.c. moist nitrogen at  $14^{\circ}$  and 749 mm.  $N = 5.88$ .

$C_{14}H_9O_3N$  requires  $N = 5.85$  per cent.



The dark alcoholic mother liquor from ethyl naphtharonylacetate, on concentration, yields a further crop of crystals of the same ester; finally, an oil remains which is fractionated under diminished pressure. The greater part distils at  $246$ — $248^{\circ}$  under 16 mm. pressure as a viscous, yellow oil. This is ethyl naphthoxyfumarate. On analysis:

0.1995 gave 0.5025  $\text{CO}_2$  and 0.1090  $\text{H}_2\text{O}$ .  $C = 68.68$ ;  $H = 6.07$ .

$C_{18}H_{18}O_6$  requires  $C = 68.79$ ;  $H = 5.73$  per cent.

In conclusion, it may be mentioned that the action of ethyl chlorofumarate on  $\alpha$ -naphthol takes place, also, at the ordinary temperature on adding to the dry sodium derivative of  $\alpha$ -naphthol a solution of the ethyl ester in absolute ether; heat is developed, the mixture turns red, and deposits a solid. After standing for several days in a flask provided with a drying tube, the product is treated as in the former case in order to separate the above-mentioned compounds.

GONVILLE AND CAIUS COLLEGE,  
CAMBRIDGE.

## XLII.—*Mesoxalic Semi-Aldehyde.*

By HENRY JOHN HORSTMAN FENTON, F.R.S., and JOHN HENRY RYFFEL,  
B.A., B.Sc.

CHLORINE and bromine have, as is well known, very little action on an aqueous solution of tartaric acid at the ordinary temperature; it is found, however, that in presence of ferrous iron the action is considerably accelerated. If the solution be saturated with chlorine, the yellow colour which is first produced soon disappears on standing, and after

some hours the odour of chlorine is no longer perceptible. On addition of phenylhydrazine acetate or hydrochloride to the solution so obtained, a bright orange-yellow precipitate is produced.

In order to study the nature of this reaction, the following method was adopted. Ordinary *d*-tartaric acid was dissolved in five to ten times its weight of water and mixed with a small quantity of freshly prepared ferrous tartrate (obtained by dissolving 'ferrum redactum' in a solution of the acid). A slow current of chlorine was then passed into the mixture until saturation appeared complete. After standing overnight, or until the odour of chlorine had disappeared, it was again saturated with the gas, and this treatment repeated until a sufficient quantity of the product had been formed, the progress of the change being ascertained by the phenylhydrazine reaction. The liquid was then concentrated to a small bulk by distillation under very reduced pressure at about 50°, and was then allowed to stand, preferably in a vacuum desiccator, until most of the unaltered tartaric acid had crystallised out. The mother liquor from these crystals remains as a thick syrup which refuses to crystallise. The product is very stable at the ordinary temperature and keeps remarkably well without apparent change, but boiling changes its character, the product then giving a small quantity of a highly crystalline, brownish precipitate when tested with phenylhydrazine.

Bromine, or hypochlorite, produces an effect similar to that of chlorine, and a very simple method of demonstrating the change is to add a small quantity of sodium hypochlorite to potassium hydrogen tartrate suspended in water and mixed with a little ferrous salt. After allowing the mixture to stand a short time and removing any excess of chlorine, if necessary, by a current of air or by sulphurous acid, the liquid gives an abundant orange-yellow precipitate with phenylhydrazine salts.

The proportion of iron used is (as in various similar oxidation processes previously described by one of the authors) not a matter of importance; the merest traces have a marked effect. In these experiments, about 1/5000 to 1/1000 part of iron to 1 part of acid was employed.

In the present case, a certain amount of action can be detected in absence of iron, but the process is then very slow and the yield poor.

The syrupy product obtained in the manner described above still contains tartaric acid, and in order to investigate its nature the action of various reagents was studied.

#### *Action of Phenylhydrazine.*

A dilute solution of the product gives the above described orange-yellow precipitate almost immediately in the cold with either the acetate or hydrochloride of phenylhydrazine. The precipitation is

accelerated by heating and is complete in half-an-hour or less. After washing with water and drying in the air, the precipitate dissolves easily in alcohol and sparingly in hot benzene or chloroform. From the latter solvent, it separates on cooling in masses of brilliant orange-golden needles or prisms. These, when quickly heated, melt usually at  $218^{\circ}$  after the first crystallisation and on further recrystallisation once or twice from the same solvent, melt constantly at  $222-224^{\circ}$ . Analysis of the product dried at  $100^{\circ}$  gave the following result:

0.1181 gave 20.1 c.c. nitrogen at  $18^{\circ}$  and 749 mm.  $N = 19.74$  per cent.

It dissolves in boiling sodium carbonate solution, and, on cooling, a beautifully crystalline sodium salt is deposited, the aqueous solution of which dyes silk, wool, &c., a bright lemon-yellow colour. Heated with acetic anhydride, it yields a substance which crystallises from alcohol in brilliant orange-red needles which melt at  $150^{\circ}$ .

The composition and properties of the product coincide in every way exactly with those of one which has previously been described in various former communications (Fenton and Jones, *Trans.*, 1900, 77, 77, and 1901, 79, 91).

It was first obtained by the further oxidation of malic acid in presence of iron, secondly by oxidation of oxalacetic acid under similar conditions, and thirdly by heating the phenylhydrazine salt of di-hydroxymaleic acid with excess of phenylhydrazine for some time on a water-bath. (The same result is also produced by heating the salt with water alone.) Analysis of the compound prepared in these ways gave  $C = 63.2$ ,  $H = 5.1$ ,  $N = 20.1$  per cent. as a mean of several concordant experiments. The nature of the compound was the subject of much investigation, since it so closely resembled the osazone of hydroxypyruvic acid, first obtained by Nastvogel from dibromopyruvic acid (*Annalen*, 1888, 248, 85), and subsequently by Will from collodion-wool (*Ber.*, 1891, 24, 400 and 3831). The same osazone was afterwards obtained by the action of phenylhydrazine on the product of oxidation of glyceric acid in presence of iron (Fenton and Jones, *Trans.*, 1900, 77, 72). There remained, however, the very considerable discrepancy in the *melting point*. The osazone of hydroxypyruvic acid melted at  $201-203^{\circ}$  (Nastvogel),  $205^{\circ}$  (Will), and  $207^{\circ}$  (Fenton and Jones); whereas the product at present under discussion melts at  $222-224^{\circ}$ .\*

In consequence of this difference, and in view of the fact that the present product of higher melting point was always obtained from

\* Friedel and Combes (*Bull. Soc. Chim.*, 1890, [iii], 3, 770) state that by adding phenylhydrazine to the product of electrolysis of tartaric acid, they obtained the osazone of glyoxal, melting at  $160^{\circ}$ , and the osazone of glyoxalcarboxylic acid, melting at  $218^{\circ}$ . They give, however, no details, analyses, or further information whatever.

acids containing 4 carbon atoms in the molecule, other possible explanations as to its nature were suggested (Fenton and Jones, *Trans.*, 1901, 79, 98). It might, for example, be the hydrazide-dihydrazone of dioxosuccinic acid, and this idea was apparently supported by the fact that when heated with acetic anhydride it gives notable quantities of carbon dioxide and aniline in addition to the phenylhydrazine-ketophenylpyrazolone of Knorr. This result might, however, be otherwise explained, and the question still remained open whether the product of higher melting point is a derivative of a 3 or 4 carbon acid. The calculated composition shows very little difference, Nastvogel's osazone,  $C_{15}H_{14}O_5N_4$ , requiring C 63.82, H 4.96, N 19.85 per cent., and the 4 carbon derivative above suggested,  $C_{22}H_{20}O_5N_6$ , requiring C 63.46, H 4.80, N 20.19 per cent.

By a numerical coincidence, the same close similarity of composition exists between the corresponding derivatives of various other hydrazines (nitrophenyl-, bromophenyl-, tolyl-hydrazine, &c.), so that it is evident that the question cannot be settled by analysis of any of these derivatives. It appeared probable, however, that a careful comparison of the properties of derivatives of these substituted hydrazines obtained from dibromopyruvic acid with those from the tartaric acid oxidation product now under discussion should give more definite information as to the question, and the following experiments were therefore made with this object.

(1) The product obtained from tartaric acid by action of chlorine, described above, was mixed with excess of *p*-bromophenylhydrazine dissolved in acetic acid. The resulting orange-coloured precipitate was washed, dried in the air, and recrystallised twice from a mixture of absolute alcohol and benzene. The long, bright orange-coloured needles so obtained melted at 245—246°.

Dibromopyruvic acid (1 mol.) was then dissolved in water and mixed with a solution of *p*-bromophenylhydrazine hydrochloride (2 mols.) and the mixture allowed to stand 3 to 4 hours at the ordinary temperature. An orange precipitate exactly similar to that last mentioned was obtained, and this, when recrystallised in a similar way, melted precisely at the same temperature, 245—246°.

(2) The tartaric acid product was mixed with an excess of *p*-tolylhydrazine hydrochloride in aqueous solution. An orange-red precipitate soon appeared, and after 3 or 4 hours was filtered off, washed, dried, and recrystallised from hot benzene. The orange-coloured needles so obtained, when slowly heated, began to soften at 188° and melted completely at 194—195°. Nastvogel (*loc. cit.*), by the action of *p*-tolylhydrazine hydrochloride on dibromopyruvic acid, obtained golden needles which melted at 186—188°.



(3) These results pointed so strongly to the identity of the products from the two different sources that it appeared desirable to prepare the *phenylhydrazine* derivative from dibromopyruvic acid exactly according to Nastvogel's directions, and to compare it with the osazone from the tartaric acid product.

The melting point of this osazone from tartaric acid, oxalacetic acid, malic acid, and dihydroxymaleic acid has been determined a very large number of times, and the results from all these different sources are remarkably concordant; it may, in fact, be taken as established that the melting point is 222—224°.

The specimens from all these sources have, for analysis, been recrystallised from *chloroform* and the melting points determined by the quick-heating method. But even slow heating does not lower the melting point more than 3° or 4°.

With regard to Nastvogel's osazone, this author does not mention how the melting point was determined, but Will determined it by the quick-heating method. But in all the methods by which this osazone has hitherto been obtained (that is, from dibromopyruvic acid, collodion-wool, and glyceric acid) the product was purified by crystallisation from *benzene*.

Nastvogel's experiment was therefore carefully repeated:—3.5 grams of phenylhydrazine hydrochloride were dissolved in water and a solution of 3 grams of dibromopyruvic acid was added, the mixture being kept cold. A bright orange precipitate began to separate almost at once, and after 3½ hours was collected, washed, dried in the air, and recrystallised three times from hot *chloroform*. The resulting product resembled in every respect the osazone from tartaric acid, &c., and melted at 222—224°.

It is therefore evident that this is the true melting point of the osazone, and it is remarkable that so many observers have obtained the lower value, the explanation being, apparently, that chloroform is the more appropriate solvent for its purification.

The above facts practically remove all doubt as to the identity of Nastvogel's osazone with that at present under discussion. Further evidence of this was obtained in the following way. The highly concentrated syrup from the oxidation product of tartaric acid was dissolved in absolute alcohol, saturated with dry hydrogen chloride, allowed to stand overnight, and distilled to small bulk under diminished pressure and the product again treated in a similar manner. It was then poured into cold water, extracted with ether, and dried over calcium chloride. After distilling off the ether, the liquid contains some ethyl tartrate and the products are difficult to separate, but on adding phenylhydrazine acetate and diluting with

water a lemon-yellow precipitate slowly separates. This, when re-crystallised, first from alcohol and then from benzene and a little light petroleum, was obtained in yellow, transparent plates which melted at 229—231°. This substance dissolves easily in hot alcohol or benzene, but is nearly insoluble in alkalis.

0.1889 gave 29.8 c.c. nitrogen at 19° and 751 mm.  $N = 18.28$ .

$C_{17}H_{18}O_2N_4$  requires  $N = 18.06$  per cent.

This product is evidently identical with that which Will obtained by the action of ethyl iodide on the osazone from collodion-wool, and is, in fact, the ethyl ester of this osazone:



The osazone,  $OH(N_2HPh) \cdot C(N_2HPh) \cdot CO_2H$ , may obviously be derived from (1) hydroxypyruvic acid, (2) the semi-aldehyde of tartronic acid, or (3) the semi-aldehyde of mesoxalic acid. The product which Will obtained from collodion-wool is considered by him to be hydroxypyruvic acid from analysis of its metallic salts and from the fact that it is not oxidised by bromine.

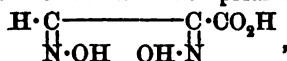
The substance obtained by Fenton and Jones by oxidation of glyceric acid in presence of iron is in many respects similar, but it gives an intense violet colour with ferric salts in presence of alkalis, a property which presumably is not possessed by Will's product, since no mention is made of it. The glyceric acid product, if it is not hydroxypyruvic acid, may possibly be the tautomeric dihydroxyacrylic acid,



The oxidation product from tartaric acid at present under discussion might, so far, be any of the above-named acids. It gives, however, when its formation is complete (see below), no colour with ferric salts in presence of alkali. It might conceivably be dichloropyruvic acid, but this is excluded by the fact that if the solution be precipitated with barium acetate, the well-washed barium salt obtained contains no chlorine, and on decomposition with dilute sulphuric acid gives, with phenylhydrazine, the same osazone as before.

#### *Action of Hydroxylamine.*

If the substance under discussion is the semi-aldehyde of mesoxalic acid, it would be expected that the action of excess of hydroxylamine should give the dioxime,  $CH(NO_2H) \cdot C(NO_2H) \cdot CO_2H$ , or dioximido-propionic acid. This oxime was obtained by Söderbaum (*Ber.*, 1892, 25, 904) by the action of hydroxylamine on dibromopyruvic acid, and was shown to exist in two forms. The 'primary' acid,



melts at 141—143°, and the 'secondary' acid,  $\begin{array}{c} \text{H} \cdot \text{C} \text{---} \text{C} \cdot \text{CO}_2\text{H} \\ | \qquad \quad | \\ \text{N} \cdot \text{OH} \quad \text{N} \cdot \text{OH} \end{array}$ , at about 172°.

If the primary acid is dissolved in the least possible quantity of ammonia, well cooled by ice, and acidified with hydrochloric acid, it is transformed into the secondary acid. Both forms give a blood-red colour with ferric chloride, and with ferrous sulphate and a little caustic soda they give an intense, but unstable, violet colour. Cupric acetate gives an olive-green precipitate.

The present tartaric acid oxidation product was concentrated as before and freed as much as possible from unaltered tartaric acid; it was then dissolved in water, mixed with excess of an aqueous solution of hydroxylamine hydrochloride, and neutralised, or nearly so, by the gradual addition of solid sodium carbonate, the mixture being cooled by ice. The solution turns dark red or violet, and on standing deposits a white sodium salt. It was allowed to stand for a few hours at 0° and then for about 24 hours at the ordinary temperature. The mixture was filtered with the aid of suction, the solid sodium salt treated with excess of dilute sulphuric acid, and extracted several times with ether. The ethereal solution was distilled to a small bulk and allowed to stand in a vacuum desiccator, when it solidified to a reddish mass. This was dissolved in the least possible quantity of ammonia, well cooled by ice, and acidified with strong hydrochloric acid.

After standing a short time, a mass of long, colourless needles separated; these were purified by redissolving in ammonia and acidifying with dilute sulphuric acid under similar conditions.

The resulting product, dried in a vacuum desiccator, when slowly heated melted at 178—180°. It is somewhat sparingly soluble in cold water and the aqueous solution behaves with ferric chloride, ferrous sulphate, and cupric acetate exactly as above described with Söderbaum's acid.

The vacuum-dried product gave the following results on analysis:

- I. 0.1571 gave 0.1551 CO<sub>2</sub> and 0.0454 H<sub>2</sub>O. C = 26.92; H = 3.21.
  - II. 0.1064 „ 18.8 c.c. nitrogen at 18° and 767 mm. N = 20.98.
- C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>N<sub>2</sub> requires C = 27.27; H = 3.03; N = 21.21 per cent.

#### *Oxidation to Mesoxalic Acid.*

The action of hydroxylamine and of phenylhydrazine practically settles the question as to the nature of the product under discussion, that it is the semi-aldehyde of mesoxalic acid. It was considered, however, that it would be satisfactory to prove the matter conclusively by oxidation of the aldehyde to mesoxalic acid.

Bromine or chlorine did not appear to be suitable agents for this purpose, owing to the presence of unaltered tartaric acid in the substance to be operated on, so that cupric oxide was selected as the most appropriate. A solution of the tartaric acid oxidation product was made alkaline with soda and mixed with excess of freshly precipitated cupric hydroxide. On warming to about  $60^{\circ}$ , a rapid reduction took place, and when this appeared to be complete the mixture was filtered, the liquid acidified with hydrochloric acid, and the copper removed by hydrogen sulphide, excess of the latter being avoided. Addition of phenylhydrazine, as acetate or hydrochloride, to this solution gave a yellow colour, and after standing a short time, a pale yellow precipitate consisting of masses of fine needles. These, when recrystallised from hot alcohol, melted at  $171-172^{\circ}$  and corresponded in properties exactly with the hydrazone of mesoxalic acid (compare Elbers, *Annalen*, 1885, 227, 341; Clemm, *Ber.*, 1898, 31, 1451; Fenton and Jones, *Trans.*, 1900, 77, 71).

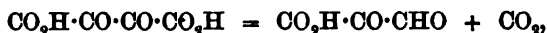
For analysis, the substance was prepared from the pure product described below and phenylhydrazine hydrochloride. Thus obtained, it was quite pure without recrystallisation. After being well washed with water and alcohol and dried in a vacuum desiccator, two distinct specimens, prepared on different occasions, melted at  $173-174^{\circ}$  and gave on analysis the following results:

- I. 0.2243 gave 25.5 c.c. nitrogen at  $14^{\circ}$  and 765 mm.  $N = 13.65$ .  
 II. 0.1910 „ 22.2 „ „  $17^{\circ}$  „ 759 mm.  $N = 13.70$ .  
 $C_9H_8O_4N_2$  requires  $N = 13.46$  per cent.

Clemm gives the melting point of mesoxalic hydrazone as  $174^{\circ}$ .

#### *Mode of Formation.*

Theoretically there are, of course, several ways in which the semi-aldehyde of mesoxalic acid might result from tartaric acid by oxidation, and experiments were made with the object of ascertaining which of these is more probable. The simple removal of one mol. of carbon dioxide from 'anhydrous' *dihydroxytartaric* acid or dioxosuccinic acid would at once afford a direct explanation,



but as yet it has not been found possible to prepare the substance from dihydroxytartaric acid; heating the acid alone, with acid and with iron salts all gave negative or unsatisfactory results. It was observed, on the other hand, that in preparing the product by the action of chlorine on tartaric acid in presence of iron in the manner above described, the liquid in the first instance always gives a notable reaction for *dihydroxymaleic* acid when tested with ferric chloride and

alkalis (compare Fenton, *Chem. News*, 1876, 33, 190; 1881, 43, 110), but after the completion of the process, by further action of chlorine and subsequent distillation, this property no longer appears. The initial change which takes place may therefore consist in the formation of dihydroxymaleic acid, and this, by further oxidation and loss of carbon dioxide, may give rise to mesoxalic semi-aldehyde,



In order to test the latter hypothesis, pure dihydroxymaleic acid was subjected to oxidation under various conditions. It was previously shown that this acid is oxidised almost quantitatively by bromine at the ordinary temperature to dihydroxytartaric acid (Trans., 1894, 67, 48), and in trying modifications of the process it was often observed that the presence of iron—the agent which was essential for the formation of dihydroxymaleic acid from tartaric acid—had a deleterious effect. In view of this fact, it seemed not improbable that, in the process at present under discussion, the ferric salt produced may be the active agent in the oxidation of dihydroxymaleic acid to mesoxalic semi-aldehyde. This supposition is entirely borne out by experiment, and the oxidation is found to take place almost quantitatively when carried out in the following way.

Crystallised dihydroxymaleic acid,  $\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ , is covered with water or *dilute* alcohol and a solution of ferric chloride or sulphate gradually added. Each drop of the ferric salt produces an intense violet-black coloration which quickly disappears, with a considerable rise of temperature. The temperature of the mixture is allowed to rise to about  $40^\circ$ , being aided by warming if necessary, and the addition of the ferric salt is continued until a further quantity no longer produces the coloration mentioned. This point is reached when the substances are present very nearly in the ratio of  $\text{C}_4\text{H}_4\text{O}_6 : 2\text{Fe}$ .

The iron is entirely reduced to the ferrous state, and the end-point may easily be demonstrated by the usual indicators. A brisk evolution of carbon dioxide occurs during the process, and the change may be expressed by the equation:



The reaction appears to take place only with ferric salts of strong acid radicles and in presence of water; if ferric acetate be used in aqueous solution, or if alcoholic ferric chloride be added to alcoholic solution of dihydroxymaleic acid, the dark violet colour produced remains quite persistent, at any rate for several hours.

In order to obtain the product free from iron, it is best to employ ferric sulphate as oxidising agent, and, after concentration in a vacuum desiccator, to precipitate the ferrous salt by alcohol and ether,

the free sulphuric acid being neutralised by the calculated amount of sodium carbonate or baryta water. By repeating the concentration and treatment with alcohol and ether, and removing the latter in a vacuum desiccator, a syrup practically free from iron is left, which gives all the reactions described above for the tartaric acid oxidation product. Phenylhydrazine acetate or hydrochloride gives the above-described osazone melting at  $222-224^{\circ}$ ; hydroxylamine gives the dioxime identical in every way with that obtained from the tartaric acid product, and oxidation with alkaline cupric hydroxide gives a large yield of mesoxalic acid.

In order to avoid the large quantity of iron salts present in the above method, a very small quantity of a ferric salt may be employed, and, as soon as reduction is complete, the resulting ferrous salt may be re-oxidised by hydrogen dioxide, the addition of the latter being continued until the change is completed. This method appears to give good results except that a small quantity of dihydroxytartaric acid may be formed at the same time, so that the use of a ferric salt only as oxidising agent is the most reliable.

The behaviour of ferric iron in the reaction here described is of much interest in throwing light upon certain processes of oxidation in presence of iron where a ferric salt has been employed (compare Fenton, *Trans.*, 1900, 77, 1296). In these cases, there is little doubt that a ferrous salt is first produced, possibly only in minute quantity, and that this determines the oxidation in the usual manner; ferric salt appears to encourage the breaking down of the resulting product with evolution of carbon dioxide.

The isolation of mesoxalic semi-aldehyde as above described leaves now only four out of the eleven possible oxidation products of glycerol which have not been obtained; mesoxalic dialdehyde being known only in the form of oxime, and tartronic semi-aldehyde and dialdehyde, and hydroxypyruvic aldehyde being unknown.

Many interesting results may be expected from a further study of this aldehyde-acid; its aldehyde hydrate may be regarded as tautomeric with the hitherto missing trihydroxyacrylic acid, which is of much interest owing to its relationship to uric acid.

A considerable part of the expenses incurred in carrying out this investigation has been defrayed by funds kindly supplied by the Government Grant Committee of the Royal Society.

### XLIII.—*The Picriminothiocarbonic Esters.*

By JAMES CODRINGTON CROCKER, B.A., Scholar of St. John's College, Cambridge.

A SHORT preliminary note on the picriminothiocarbonic esters has already appeared (*Camb. Univ. Rep.*, 1902, 32, 23, 549), but in view of the publication of a paper dealing with the action of acidic thiocyanates on alcohol (Dixon, *Trans.*, 1902, 81, 168), it seems advisable to publish the work in full. The experiments deal entirely with the action of picryl chloride on thiocyanates and alcohols. The reaction is a remarkable one, and takes place, in most cases, with ease, the products being beautifully crystallised bodies. The first case investigated was the reaction of picryl chloride on ammonium thiocyanate in ethyl alcohol solution.

#### *Ethyl Picryl Picriminothiocarbonate.*

Ten grams of picryl chloride dissolved in hot absolute alcohol were mixed with a hot alcoholic solution of 3·2 grams of ammonium thiocyanate. Precipitation immediately took place, and a yellow oil sank to the bottom and later solidified to a yellow solid. The whole mass was filtered on cooling, washed with alcohol, water, and lastly with alcohol again. The yield was 10 grams, and the mother liquor contained free hydrochloric acid. On crystallisation from ethyl alcohol and glacial acetic acid (1:1), 8 grams of the pure substance were obtained. It forms golden-yellow, compact prisms melting at 138°. It is insoluble in water or ether, and sparingly soluble in alcohol, but easily so in benzene or acetic acid. Analysis gave the following results:

0·2049	gave	0·2566	CO <sub>2</sub>	and	0·0352	H <sub>2</sub> O.	C = 34·15 ;	H = 1·91.
0·2152	„	34·6	c.c. moist nitrogen at 17° and 755 mm.				N = 18·53.	
0·2107	„	34·8	c.c.	„	20°	„	759 mm.	N = 18·87.
0·2001	„	0·0910	BaSO <sub>4</sub> .				S = 6·24.	
C <sub>15</sub> H <sub>9</sub> O <sub>15</sub> N <sub>7</sub> S requires C = 34·16 ; H = 1·71 ; N = 18·59 ; S = 6·07 per cent.								

The substance probably contains two picryl groups. On boiling it with very concentrated aqueous potash, ammonia was evolved and ethyl alcohol was found in the distillate; it must thus contain an ethoxy-group. This was shown quantitatively by the Zeisel method. The whole apparatus was kept at 85—90°, and an additional bulb containing dilute copper sulphate was interposed to retain the sulphur-

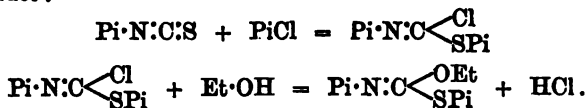
etted hydrogen formed during the reaction. The result shows that one ethoxy-group is present.

0.2575 gave 0.1107 AgI.  $\text{OEt} = 8.23$ .

$\text{C}_{13}\text{H}_4\text{O}_{12}\text{N}_7\text{S}\cdot\text{OEt}$  requires  $\text{OEt} = 8.54$  per cent.

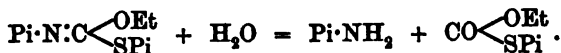
The substance is only oxidised with difficulty, and is recovered practically unchanged after boiling for two hours with a 10 per cent. solution of chromic acid in glacial acetic acid. If boiled for two hours with a mixture of glacial acetic acid and hydrochloric acid, hydrolysis takes place, and after dilution and decolorisation of the resulting liquor, picramide is deposited on cooling in bluish-yellow crystals melting at  $188^\circ$ . The yield of picramide was about 25 per cent. of the ethoxy-compound taken.

These facts gave a clue to the structure of the substance. It must contain two picryl groups, one of which is attached to a nitrogen atom, forming a picrimino-group,  $\text{Pi}\cdot\text{N}\cdot$ , the other being attached to the sulphur atom. The reaction is doubtless connected with the remarkable property which picryl derivatives possess of forming additive compounds, since neither phenyl thiocyanate nor phenylthiocarbimide reacts with picryl chloride and alcohol. The formation is explained by the equations, picryl thiocarbimide,  $\text{Pi}\cdot\text{N}\cdot\text{C}\cdot\text{S}$ , being regarded as the first product:



The alternative explanation, involving the formation of a *pseudo*-thiourethane,  $\text{Pi}\cdot\text{N}\cdot\text{C}(\text{OEt})\cdot\text{SH}$ , by the addition of a mol. of the alcohol to the thiocarbimide, is rendered improbable in view of the fact that picryl chloride is not decomposed by boiling with water or alcohol. Much less likely is it, then, to act on a SH-group. On the other hand, ethyl chlorocarbonate is easily decomposed by water or alcohol. This renders it very probable that the ethyl picrimino-chlorothiocarbonate—which in addition contains two strongly acidic picryl groups—will easily react with alcohols.

The hydrolysis to picramide is easily understood from the following equation:



When hydrolysed with potash, the picramide first formed is decomposed by the alkali into ammonia and potassium picrate.

The action of picryl chloride and ammonium thiocyanate has been tried on other alcohols with similar results. It was somewhat unexpected, however, to discover two isomeric methoxy-compounds



easily transformable one to the other. The more stable form, the " $\beta$ -isomeride," is obtained in the usual way.

*Methyl Picryl Picriminothiocarbonates.*

Ten grams of picryl chloride were dissolved in hot methyl alcohol and mixed with a solution of 3.2 grams of ammonium thiocyanate in methyl alcohol; immediate precipitation took place, and on cooling the crumbling mass was filtered off. The yield amounted to 9.2 grams, and the mother liquor contained free hydrochloric acid. The crude product may be crystallised from a mixture of glacial acetic acid and methyl alcohol (1:1); it is then obtained in fine, fluffy needles, melting constantly at  $169^{\circ}$ , which are insoluble in water or ether, slightly soluble in alcohol, and easily so in benzene or glacial acetic acid. Analysis confirmed the view that the substance was *methyl picryl picriminothiocarbonate*:

0.2027 gave 0.2437  $\text{CO}_2$  and 0.0319  $\text{H}_2\text{O}$ .  $\text{C} = 32.78$ ;  $\text{H} = 1.75$ .

0.2534 ,, 40.8 c.c. moist nitrogen at  $14^{\circ}$  and 769 mm.  $\text{N} = 19.18$ .

0.2245 ,, 0.1004  $\text{BaSO}_4$ .  $\text{S} = 6.14$ .

$\text{C}_{14}\text{H}_7\text{O}_{13}\text{N}_7\text{S}$  requires  $\text{C} = 32.75$ ;  $\text{H} = 1.37$ ;  $\text{N} = 19.10$ ;  $\text{S} = 6.24$  per cent.

The methoxy-group was determined by the Zeisel method in the usual manner, except for the addition to the apparatus of a bulb of dilute copper sulphate solution to absorb the sulphuretted hydrogen formed. The result indicates that one methoxy-group is present in the molecule:

0.2679 gave 0.1322  $\text{AgI}$ .  $\text{OCH}_3 = 6.51$ .

$\text{C}_{13}\text{H}_4\text{O}_{12}\text{N}_7\text{S} \cdot \text{OCH}_3$  requires  $\text{OCH}_3 = 6.04$  per cent.

The  $\alpha$ -isomeride which was first discovered is prepared from the  $\beta$ -compound; for this purpose, 5 grams of the  $\beta$ -isomeride are crystallised from 140 c.c. of a mixture of ethyl alcohol and acetic acid (1:1). The crystallisation is carefully watched. Minute, compact prisms are deposited at first. Immediately the  $\beta$ -isomeride begins to separate in fluffy aggregates, the mother liquor is poured off from the crystals, which are washed with alcohol and then with ether. The yield of the  $\alpha$ -isomeride obtained by this means amounts to 1.2 grams. The substance consists of compact, golden-yellow prisms, so like the ethoxy-compound in appearance as to be almost indistinguishable from it. It melts at  $158^{\circ}$ , is insoluble in water or ether, sparingly soluble in alcohol, and easily so in benzene or acetic acid. It is perfectly stable in the dry state and may be preserved for months unchanged, but in contact with solvents it is slowly but completely converted to the  $\beta$ -isomeride. The analyses indicate that the substance is *methyl picryl picriminothiocarbonate*:

0.2042 gave 0.2471  $\text{CO}_2$  and 0.0291  $\text{H}_2\text{O}$ .  $\text{C} = 33.01$ ;  $\text{H} = 1.58$ .

0.2035 „ 0.2439  $\text{CO}_2$  „ 0.0302  $\text{H}_2\text{O}$ .  $\text{C} = 32.68$ ;  $\text{H} = 1.65$ .

0.1536 „ 25.3 c.c. moist nitrogen at  $18^\circ$  and 767 mm.  $\text{N} = 19.21$ .

0.2160 „ 0.0912  $\text{BaSO}_4$ .  $\text{S} = 5.80$ .

$\text{C}_{14}\text{H}_7\text{O}_{12}\text{N}_7\text{S}$  requires  $\text{C} = 32.75$ ;  $\text{H} = 1.37$ ;  $\text{N} = 19.10$ ;  $\text{S} = 6.24$  per cent.

The presence of a methoxy-group was shown quantitatively by the Zeisel method :

0.2106 gave 0.0962  $\text{AgI}$ .  $\text{OCH}_3 = 6.03$ .

$\text{C}_{13}\text{H}_4\text{O}_{12}\text{N}_7\text{S} \cdot \text{OCH}_3$  requires  $\text{OCH}_3 = 6.04$  per cent.

That the two substances are not polymeric was shown by the identity of the molecular weights in benzene solution. Owing to the slight solubility in cold benzene, only one reading could be taken in each determination.

*$\alpha$ -Isomeride :*

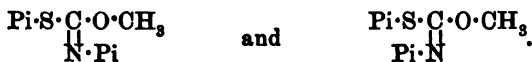
0.1693 gram lowered the freezing point of 21.67 grams of benzene by  $0.075^\circ$ . Mol. wt. = 510.

*$\beta$ -Isomeride :*

0.0823 gram lowered the freezing point of 16.73 grams of benzene by  $0.048^\circ$ . Mol. wt. = 502.

The calculated mol. wt. is 513.

These are probably not desmotropic forms, because they are perfectly stable in the dry state. On the other hand, the ease with which they can be transformed, one to the other, in solution shows that they are very probably stereoisomerides of the oxime type. Two isomeric forms are possible, represented by the expressions :



The fact that isomerides of the other homologues have not been prepared is not surprising when the limited means applicable in the particular case of these substances is considered. When melted, they decompose, and even when kept at about  $130^\circ$  for some time they are in most cases completely charred, owing to the high percentage of nitro-groups contained in them.

*n-Propyl Picryl Picriminothiocarbonate.*

2.5 grams of picryl chloride are dissolved in 10 c.c. of *n*-propyl alcohol and mixed with a hot solution of 0.8 gram of ammonium thiocyanate in 10 c.c. of *n*-propyl alcohol. A flocculent precipitate at once forms. On cooling, this is filtered from the mother liquor—which

is again found to be acid—washed with alcohol, water, and lastly with alcohol again. The yield amounted to 2 grams. The product was crystallised from alcohol and acetic acid (1:1). The pure substance melts at 151—152°. It forms lustrous, golden-yellow leaflets, insoluble in water or ether, sparingly soluble in alcohol, fairly easily so in benzene, and easily so in acetic acid. Analysis indicated that the substance was *propyl picryl picriminothiocarbonate*:

0.1861 gave 0.2408  $\text{C}_2\text{O}$  and 0.0360  $\text{H}_2\text{O}$ .  $\text{C} = 35.29$ ;  $\text{H} = 2.15$ .

0.2323 „ 36.4 moist nitrogen at 16° and 745 mm.  $\text{N} = 17.89$ .

0.2424 „ 0.1049  $\text{BaSO}_4$ .  $\text{S} = 5.94$ .

$\text{C}_{16}\text{H}_{11}\text{O}_{18}\text{N}_7\text{S}$  requires  $\text{C} = 35.49$ ;  $\text{H} = 2.03$ ;  $\text{N} = 18.11$ ;  $\text{S} = 5.92$  percent.

*iso-Butyl Picryl Picriminothiocarbonate.*

2.5 grams of picryl chloride dissolved in 10 c.c. of *isobutyl* alcohol are mixed with a hot solution of 0.8 gram of ammonium thiocyanate in 20 c.c. of *isobutyl* alcohol. The mass becomes almost solid from the deposition of minute plates. On cooling, the precipitate is filtered off from the acid mother liquor. The yield amounts to 2.4 grams. After washing with alcohol, water, &c., the product is crystallised from a mixture of acetic acid and alcohol (1:1). The new substance melts at 173° and consists of golden-yellow, lustrous leaflets, which are insoluble in water or ether, but easily soluble in acetic acid. Analysis showed it to be *isobutyl picryl picriminothiocarbonate*:

0.2288 gave 0.3080  $\text{CO}_2$  and 0.0448  $\text{H}_2\text{O}$ .  $\text{C} = 36.72$ ;  $\text{H} = 2.17$ .

0.1971 „ 29.9 c.c. moist nitrogen at 16° and 765 mm.  $\text{N} = 17.80$ .

0.2194 „ 33.4 „ „ 15° „ 760 mm.  $\text{N} = 17.83$ .

$\text{C}_{17}\text{H}_{13}\text{O}_{18}\text{N}_7\text{S}$  requires  $\text{C} = 36.77$ ;  $\text{H} = 2.34$ ;  $\text{N} = 17.66$  per cent.

Similar compounds have been obtained with *isopropyl*, *allyl*, and *benzyl* alcohols, and the investigation of these is being proceeded with. The ease with which this reaction takes place makes it probable that it will be of use for the characterisation and identification of the lower alcohols; in most cases, it takes place easily, even when the alcohol is diluted with benzene.

In conclusion, I have to thank Dr. G. S. Turpin for his kindness in permitting me to start this work, which is the result of an observation made by him in 1891.

UNIVERSITY LABORATORY,  
CAMBRIDGE.

XLIV.—*Isomeric Additive Compounds of Dibenzyl Ketone and Deoxybenzoin with Benzylidene-p-toluidine, m-Nitrobenzylideneaniline, and Benzylidene-m-nitraniline. Part III.*

By FRANCIS E. FRANCIS, B.Sc., Ph.D.

EXPERIMENTS similar to those carried out with dibenzyl ketone and benzylideneaniline (Trans., 1899, 75, 865; 1900, 77, 1191) were tried with this ketone and the benzylidene-*o*-toluidine and *p*-toluidine. As previously mentioned, the former substance does not appear to give additive compounds with dibenzyl ketone, whereas the latter readily reacts with it and with deoxybenzoin.

The dibenzyl ketone benzylidene-*p*-toluidines isolated were similar to those obtained in the case of dibenzyl ketone benzylideneaniline, but apparently much less stable; the  $\alpha$ -modification, melting at 163°, is converted into what is presumably the  $\beta$ -form melting at 174° by recrystallisation from benzene containing traces of phenylhydrazine, and although it may be recrystallised several times under these conditions, its melting point falls to 163° if pure benzene is employed. A similar change takes place on treating the modification melting at 174° with traces of sodium ethoxide, when a substance melting at 182° is obtained, but again the melting point of this falls to 163° on recrystallisation. With regard to deoxybenzoin benzylidene-*p*-toluidine, great difficulty was experienced in obtaining more than very small amounts of the  $\alpha$ -product owing, apparently, to its instability. A modification of high melting point and slight solubility was simultaneously produced from the mixture of deoxybenzoin and benzylidene-*p*-toluidine, and if the temperature was high enough, this was the only product formed. As it was desired, if possible, to obtain confirmation of the work that had been previously carried out, the further investigation of these substances was abandoned.

*m*-Nitrobenzylideneaniline was next employed, but the additive compound obtained with it and dibenzyl ketone turned out to be a mixture of two substances which could only be separated in the pure state in small amount and with considerable difficulty. The product possessing the lower melting point was apparently similar to the  $\alpha$ -modifications previously described, the  $\beta$ -form obtained from it in the usual way by recrystallisation from benzene containing traces of piperidine showed a melting point 31° higher; this was regarded as a satisfactory confirmation of previous results where the melting points of the  $\beta$ -modifications had never been more than 10–11° higher than those of the  $\alpha$ -forms. On the other hand, traces of sodium ethoxide

which had previously given rise to the  $\gamma$ -modifications of higher melting point than  $\beta$ -forms had but slight effect on either the  $\alpha$ - or  $\beta$ -forms, and no substance of constant melting point could be isolated.

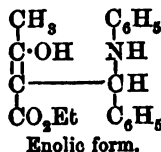
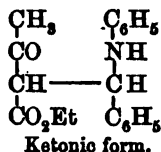
The product having the higher melting point, produced with the  $\alpha$ -modification and separated from it by its lesser solubility in dilute acetone, had the same molecular weight. Its melting point was within a few degrees of that of the  $\beta$ -form, but since its hydrochloride was different and its melting point was raised  $10^\circ$  by recrystallisation from benzene containing piperidine, it was presumably a different modification.

The difficulty found in obtaining a sufficient quantity of these substances led to similar experiments being tried with benzylidene-*m*-nitraniline, and, unlike the isomeric *m*-nitrobenzylideneaniline, this gave a pure additive compound with dibenzyl ketone. The resulting  $\alpha$ -dibenzyl ketone benzylidene-*m*-nitraniline was a stable, reddish-yellow, crystalline substance, and from it the  $\beta$ -modification was obtained with rather more difficulty than had been previously experienced, but when obtained had strikingly different characteristics. Although its molecular weight was identical with that of the  $\alpha$ -modification, its melting point was  $43^\circ$  higher, and its crystalline form and greenish-yellow colour, together with its lesser solubility in the ordinary solvents, sharply differentiated it from that modification. It was also unaffected by heat, whereas most of these modifications are reconverted into the more stable  $\alpha$ -form. A very similar change to this takes place when the  $\alpha$ -modification is recrystallised from benzene containing traces of sodium ethoxide; the substance obtained was, in appearance, solubility, and stability towards heat, very similar to the  $\beta$ -form, and only differed from it in having a slightly higher melting point,  $182$ — $183^\circ$ , as compared with  $177$ — $178^\circ$ . In previous cases, it had been possible to further identify the different modifications by means of their hydrochlorides, but in this instance they were too unstable for this purpose.

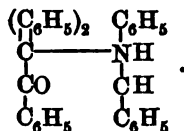
The correspondence between  $\alpha$ - and  $\beta$ -dibenzyl ketone benzylidene-*m*-nitraniline and  $\alpha$ - and  $\beta$ -dibenzyl ketone *m*-nitrobenzylideneaniline is close, and the distinction between the  $\alpha$ - and  $\beta$ -modifications of each very much more marked than between any of those previously investigated, and sufficient finally to settle the individuality of the so-called  $\beta$ -forms. As regards the  $\gamma$ -modifications, the investigations described have not been so satisfactory; however, if the compound obtained from  $\alpha$ -dibenzyl ketone benzylidene-*m*-nitraniline corresponds to it, and it seems hardly likely that piperidine and sodium ethoxide should give rise to the same substances, then the previous statement about the  $\beta$ - is equally true about the  $\gamma$ -modifications. It is hoped that further investigation will also settle this

point. The substances of higher melting point which have been produced in addition to the  $\alpha$ -additive compounds in the case of benzylideneaniline and deoxybenzoin (but not further investigated for want of material), benzylidene-*p*-toluidine, and deoxybenzoin, *m*-nitrobenzylideneaniline, and dibenzyl ketone and without the  $\alpha$ -modification in the case of benzylidene-*m*-nitraniline and deoxybenzoin, appear to be similar in molecular weight and composition to the modifications described in this and previous papers as  $\alpha$ -,  $\beta$ -, and  $\gamma$ -forms. The inability so far to obtain sufficient quantities of these substances makes it very difficult to investigate them further or to be able to state whether or no the addition of the benzylideneaniline or its derivatives to the ketone has taken place in the same manner as with the other modifications.

An attempt is now being made to prepare such a ketone as diphenylacetophenone, for the following reason. According to Schiff, the constitution of the substances obtained from ethyl acetoacetate and benzylideneaniline may be formulated in the following manner:



Unlike ethyl acetoacetate, diphenylacetophenone, or a similar ketone having one OH- but no OH<sub>2</sub>- group, should react only in one way, that is, it should give rise to a ketonic modification as sole product,



It is hoped that this investigation may throw some light on the substances described in this and previous papers, and indicate whether or no they are similarly constituted to the additive products obtained by Schiff from ethyl acetoacetate.

#### EXPERIMENTAL.

##### *Dibenzyl Ketone and Benzylidene-*p*-toluidine.*

(i)  *$\alpha$ -Dibenzyl Ketone Benzylidene-*p*-toluidine.*—When molecular proportions of dibenzyl ketone and benzylidene-*p*-toluidine are kept at 60° for 48 hours, this substance separates out. It is purified by washing with light petroleum and recrystallisation from boiling benzene; the final yield of pure product was small. It is a white, crystalline sub.

stance, showing a constant melting point of  $164^{\circ}$ , soluble in hot, and to a less extent in cold benzene, and recrystallising unchanged from boiling alcohol, in which it is only slightly soluble. On analysis, the following results were obtained :

Found C = 85.89 ; H = 6.89.

$C_{20}H_{27}ON$  requires C = 85.92 ; H = 6.66 per cent.

*$\alpha$ -Hydrochloride*,  $C_{20}H_{27}ON.HCl$ .—If the  $\alpha$ -additive product is dissolved in excess of benzene and dry hydrogen chloride passed in, the salt separates out as a white, crystalline mass melting at  $143^{\circ}$ . It is dissociated by water, giving the  $\alpha$ -base melting at  $164^{\circ}$ , and, unlike the corresponding hydrochloride of dibenzyl ketone benzylideneaniline, which is partially converted into the  $\gamma$ -base, it is dissociated by absolute alcohol, yielding the unchanged  $\alpha$ -base melting at  $164^{\circ}$ .

On analysis, the following result was obtained :

HCl found 8.05 ; calculated 8.26 per cent.

(ii)  *$\beta$ - and  $\gamma$ -Dibenzyl Ketone Benzylidene-*p*-toluidine*.—Unlike the previously described compounds, the  $\alpha$ -form does not appear to be converted into the  $\beta$ -modification by piperidine in benzene solution, but if the  $\alpha$ -form is recrystallised from benzene containing a trace of phenylhydrazine, a substance which appears to be the unstable  $\beta$ -modification melting at  $174$ — $175^{\circ}$  separates out. This may be recrystallised from benzene containing traces of phenylhydrazine and shows an unchanged melting point, but if the substance be recrystallised several times from pure benzene its melting point falls to  $164^{\circ}$ , that is, it is reconverted into the more stable  $\alpha$ -modification. The following results were obtained on analysis :

Found C = 85.89 ; H = 6.92.

$C_{20}H_{27}ON$  requires C = 85.92 ; H = 6.66 per cent.

If this modification, which is more unstable than any of those previously described, is dissolved in benzene and treated with traces of sodium ethoxide, it is precipitated unchanged by light petroleum after standing for 5 or 6 hours, but if kept at a temperature of  $50^{\circ}$  for 12 hours, the product then obtained by the same means shows a distinctly higher melting point, namely,  $181$ — $182^{\circ}$ , but on recrystallising the substance from pure benzene this gradually drops to  $164^{\circ}$ , the melting point of the  $\alpha$ -modification. There appears to be some indication, therefore, of the existence of a  $\gamma$ -modification, but both this and the  $\beta$ - were so unstable that further work upon them was abandoned.

*Deoxybenzoin and Benzylidene-p-toluidine.*

When molecular quantities of these substances were allowed to remain at 50° for 2 days, great difficulty was experienced in separating the additive compounds formed. A partial resolution into two fairly pure modifications was effected by benzene, the substance possessing the higher melting point being much less soluble than the other. The latter, of which only small quantities were obtained, could be recrystallised from benzene and light petroleum, and showed a fairly constant melting point of 147°, but from its crystalline appearance it was evidently impure; it corresponds, apparently, to the  $\alpha$ -modification, and on melting appeared to be partially converted into the substance of higher melting point. It gave the following results on analysis:

Found C = 85.21; H = 6.58.

$C_{25}H_{25}ON$  requires C = 85.93; H = 6.39 per cent.

The substance of higher melting point can be obtained without the  $\alpha$ -modification by keeping the mixture of benzylidene-*p*-toluidine and deoxybenzoin between 65° and 70° during the condensation, and on recrystallisation from boiling toluene melted sharply at 191°. It can be recrystallised unchanged from toluene containing traces of piperidine. A determination of the molecular weight in pyridine solution gave 410, as compared with 391, the calculated value. It evidently corresponds to the similar substance obtained from benzylideneaniline and deoxybenzoin and to others described in this paper.

It gave the following results on analysis:

Found C = 85.58; H = 6.65.

$C_{25}H_{25}ON$  requires C = 85.93; H = 6.39 per cent.

*Dibenzyl Ketone and m-Nitrobenzylideneaniline.*

(i)  *$\alpha$ -Dibenzyl Ketone m-Nitrobenzylideneaniline.*—When the ketone and base are mixed in molecular proportion and kept at a temperature of 50–60°, this substance, together with another of much higher melting point, slowly separates out. The removal of the  $\alpha$ -modification from this mixture is best effected by fractional crystallisation from dilute acetone, or, with more difficulty, from chloroform and light petroleum; the yield of pure  $\alpha$ -product melting at 147° is small. It is a light yellow, crystalline powder, soluble in benzene or chloroform, and best recrystallised from benzene or light petroleum. It is not affected by recrystallisation from boiling alcohol, and may be rapidly melted without change. It gave the following results on analysis:

Found C = 77.42; H = 5.84.

$C_{28}H_{24}O_2N_2$  requires C = 77.06; H = 5.50 per cent.



It is slightly basic, but judging from the instability of the hydrochloride obtained by passing dry hydrogen chloride into a benzene solution of the base, the introduction of the nitro-group has weakened the basicity. The *hydrochloride* is a white, crystalline powder, melting between 136° and 137°, and rapidly dissociating, even in dry air, into the  $\alpha$ -base and hydrogen chloride.

The substance possessing the higher melting point obtained, with the  $\alpha$ -modification as described above, can be obtained pure by recrystallisation from pure benzene. It melts at 179—180°, and is a yellow, crystalline mass, less soluble in benzene than the  $\alpha$ -form. A determination of the molecular weight in benzene solution gave 412 and 409 instead of 436, the calculated value. It slowly melts if kept for 11 minutes at 147°, the melting point of the  $\alpha$ -modification. If crystallised from benzene containing traces of piperidine; its melting point rises to 188—189°. It gave the following results on analysis:

Found C = 77.39; H = 5.78; N = 6.40.

$C_{28}H_{24}O_3N_2$  requires C = 77.06; H = 5.50; N = 6.42 per cent.

The *hydrochloride* obtained in the usual way is a white, crystalline powder melting at 148—149°, and is dissociated by water, giving back the base melting at 177—178°. It gave the following result on analysis:

Found HCl = 7.40.

$C_{28}H_{24}O_3N_2$  requires HCl = 7.72 per cent.

(ii)  *$\beta$ -Dibenzyl Ketone m-Nitrobenzylideneaniline*.—When the  $\alpha$ -additive compound is recrystallised from benzene containing traces of piperidine, this substance separates out as a light yellow, crystalline mass. It can be purified by recrystallisation from benzene or chloroform, and shows a constant melting point of 178—179°, that is, 31° higher than the  $\alpha$ -modification. It recrystallises unchanged from acetone or absolute alcohol, and may be rapidly melted without decomposition or change. If kept at 147°, the melting point of the  $\alpha$ -form, for 18 minutes it melts, that is, the transformation required 7 minutes longer than in the case of the substance described above, with a nearly similar melting point. It gave the following results on analysis:

Found C = 77.06; H = 5.61.

$C_{28}H_{24}O_3N_2$  requires C = 77.06; H = 5.50 per cent.

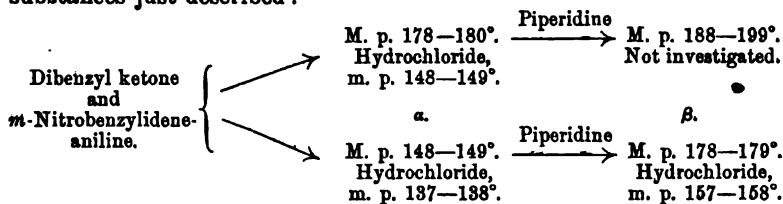
The  *$\beta$ -hydrochloride*, obtained as previously described, is a white, crystalline powder melting at 158°, and easily dissociated by water or alcohol, giving back the  $\beta$ -form melting at 178—179°. It gave the following result on analysis:

Found HCl = 7.68.

$C_{28}H_{24}O_3N_2$ , HCl requires HCl = 7.72 per cent.

(iii) When an attempt was made to obtain the  $\gamma$ -modification by means of sodium ethoxide, it was only found possible to raise the melting point of the  $\alpha$ -modification from  $147^\circ$  to  $153^\circ$ , and it appeared impossible to change the  $\alpha$ -form completely into a substance with constant melting point; this was equally true of the  $\beta$ -modification.

The following diagram illustrates the relationships between the substances just described :



*Dibenzyl Ketone and Benzylidene-m-nitraniline.*

(i)  *$\alpha$ -Dibenzyl Ketone Benzylidene-m-nitraniline.*—The preparation of this substance was carried out in the usual manner, but a much longer time, between seven and ten days, at  $40-50^\circ$  was required before the  $\alpha$ -additive product separated out. It was purified by recrystallisation from benzene and light petroleum, and the yield obtained was much larger than with any of the substances previously described. It crystallises in long, reddish-yellow needles melting at  $134-135^\circ$ , and may be recrystallised unchanged from boiling alcohol or acetone; it may also be rapidly melted without decomposition taking place. Determinations of the molecular weight in benzene solution gave 459 and 440 instead of 436, the calculated value. The hydrochloride, a white, crystalline mass with indefinite melting point, is very unstable and rapidly dissociates into hydrogen chloride and the free base.

On analysis, the following results were obtained :

Found C = 77.15 ; H = 5.82.

$C_{25}H_{24}O_3N_2$ , requires C = 77.06 ; H = 5.50 per cent.

(ii)  *$\beta$ -Dibenzyl Ketone Benzylidene-m-nitraniline.*—If the  $\alpha$ -modification is dissolved in excess of benzene and rather more piperidine added than on previous occasions, the  $\beta$ -form separates out slowly in two or three days. It is only very slightly soluble in cold benzene. It is a greenish-yellow, crystalline mass melting at  $177-178^\circ$ , or  $43^\circ$  higher than the  $\alpha$ -modification. It remains unaltered when kept for one hour at  $134-135^\circ$ , the melting point of the  $\alpha$ -form, and on raising the temperature melts sharply at  $177-178^\circ$ ; it may also be rapidly melted without decomposition or change taking place. A determination of the molecular weight in benzene solution gave 483 as compared with 436, the calculated value. There is no evidence of the formation of

any molecular compound between the  $\alpha$ - and  $\beta$ -modifications, since on mixing equal quantities of the two and dissolving in boiling benzene, the  $\beta$ -form separates out on cooling, and from the filtrate, addition of light petroleum throws out the  $\alpha$ -modification in a nearly pure state. Like all other substances of this class so far investigated, it gave no colour reaction with ferric chloride.

The following results were obtained on analysis :

Found C = 77.16 ; H = 5.80.

$C_{28}H_{24}O_8N_2$  requires C = 77.06 ; H = 5.50 per cent.

(iii)  *$\gamma$ -Dibenzyl Ketone Benzylidene-m-nitraniline.*—When the  $\alpha$ -modification is allowed to stand for several days in benzene solution containing traces of sodium ethoxide, the substance which slowly crystallises out resembles in appearance, crystalline form, and solubility, the  $\beta$ -modification. The melting point is 182—183°, compared with 177—178° of the latter, and, up to the present, with the exception of this, no other points of difference have been found between them. The hydrochloride, which is as unstable as that of the  $\beta$ -modification, has too indefinite a melting point to serve as a method of distinguishing between them. The additive product gave the following results on analysis :

Found C = 77.51 ; H = 5.81.

$C_{28}H_{24}O_8N_2$  requires C = 77.06 ; H = 5.50 per cent.

*Deoxybenzoin and Benzylidene-m-nitraniline.*

Although molecular quantities of these substances were kept for 12 days between 30° and 40°, no additive product separated, but on raising the temperature to 70° the mass slowly solidified. The product was purified by recrystallisation from large quantities of boiling benzene or from boiling toluene ; it was a greenish-yellow, crystalline mass melting at 208°. A determination of the molecular weight in benzene solution gave 412 instead of 422, the calculated value. The following results were obtained on analysis :

Found C = 77.13 ; H = 5.51.

$C_{27}H_{22}O_8N_2$  requires C = 76.77 ; H = 5.21 per cent.

Judging from its high melting point, slight solubility, and the fact that it can be recrystallised unchanged from benzene containing piperidine, this substance appears to be analogous to the other isomerides of high melting point which have been previously described.

*Summary.*

The following table gives the results which have been so far obtained. The difference between the reaction of the two ketones, deoxybenzoin and dibenzyl ketone, with benzylidene-*m*-nitraniline is remarkable :

Ketone.	Benzylidene-aniline derivative.	$\alpha$ .	Product of high m. p. obtained with the $\alpha$ -form.	$\beta$ .	$\gamma$ .
Dibenzyl ketone	Benzylideneaniline	164.5°	—	174.5°	182.5°
"	{ Benzylidene- <i>p</i> -toluidine }	164	—	174—175°	181—182
"	{ <i>m</i> -Nitrobenzylideneaniline }	147	179—180°	178—179	—
"	{ Benzylidene- <i>m</i> -nitraniline }	134—135	—	177—178	182—183
Deoxybenzoin	Benzylideneaniline	154°	—	164—5°	173—174°
"	{ Benzylidene- <i>p</i> -toluidine }	147	191°	?	?
"	{ Benzylidene- <i>m</i> -nitraniline }	nil	208	—	—

My thanks are due to Mr. Ludlam for his determinations of the molecular weights given in this paper. The method employed was a modification of Landsberger's, which he proposes shortly to communicate to the Society.

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## XLV.—*The Bases contained in Scottish Shale Oil.* *Part I.*

By FREDERIC CHARLES GARRETT and JOHN ARMSTRONG SMYTHE.

ALTHOUGH many workers have examined the basic substances contained in coal tar, very few have investigated those found in the crude oil obtained by the distillation of bituminous shale. Greville Williams examined the tar from Dorsetshire shale in 1855 (*Q. J. Chem. Soc.*, 7, 97), and G. Carr Robinson obtained some quinoline bases from Scottish shale oil (*Trans. Roy. Soc. Edin.*, 1879, 28, 561; 1880, 29, 265 and 273), but in 1897, George Beilby (*J. Soc. Chem. Ind.*, 1899, 16, 886) pointed out that practically nothing is known on this subject, and that in view of the fact that from seven to ten million

gallons of "basic tar" are obtained in Scotland alone during the year, it is very desirable that this tar should be fully investigated.

The "crude oil" obtained by distilling the shale undergoes a second distillation in large iron retorts, and the distillate is divided into two portions known as "green naphtha" (the more volatile portion) and "green oil" (the less volatile portion); towards the close of the distillation, a red heat is attained and a considerable quantity of "still coke" is left in the retort. The oils are then treated with strong sulphuric acid (about two per cent.), which gives a thick, black tar, and removes almost the whole of the nitrogenous compounds from the oil; after washing to remove the excess of sulphuric acid, this tar is either burnt under the boilers or thrown away as rubbish. In the extraction of the pyridine bases from coal tar, the best results are obtained by washing the "light oil" with dilute sulphuric acid, and we therefore asked Mr. D. R. Steuart of Broxburn—whom we have to thank for the great trouble he has taken in order to supply us with whatever material we have needed—to have some of the "green naphtha" treated in this way. Some 200 gallons of "green naphtha" were washed with weak sulphuric acid (one volume of acid in nine of water), giving about 5 gallons of a thin, brown-red, foul-smelling liquid of sp. gr. 1.13. This acid liquor was heated almost to boiling and steam blown through for 6 to 12 hours to remove small quantities of a dark oil having a most offensive smell; it was then made strongly alkaline by solid caustic soda (200 grams per litre), and superheated steam blown through until all the volatile bases had been driven over. The distillation proceeded rapidly at first, but slowly afterwards, and a considerable volume of distillate was obtained; from this, the basic oil was separated as completely as possible, and the aqueous portion distilled until about one-fourth had passed over; this second distillate was then made strongly alkaline by caustic soda, the bases removed and added to the first portion, and the whole dried over caustic potash. The yield amounted to about 120 grams per litre of acid liquor, about 3 kilograms being obtained in all. The mixture of bases was then fractionally distilled, using a "rod and disc" still head of twenty discs, the receiver being changed as a rule every five degrees, and the whole quantity being worked over seven times.

The yield was as follows:

Below 120° .....	0.3 per cent.
120—160 .....	13.4 "
160—200 .....	43.2 "
Above 200 .....	43.1 "
	<hr/>
	100.0 "

It was thought desirable to compare the bases obtained from the "green naphtha" with those from the "green oil," and therefore 20 gallons of each liquid were treated with dilute sulphuric acid (1 lb. of vitriol in 1 gallon of water) and worked up as already described, the bases, however, being fractionally distilled only twice.

The "green naphtha" yielded 226·3 grams of base, of which 63 per cent. boiled below 200°, whilst the "green oil" only gave 120 grams, of which 40 per cent. boiled below 200°. We are indebted to Mr. Arnold Merrick and Mr. W. Saunderson for their assistance in making this comparison.

Only those portions boiling below 164° have been examined as yet, the plan adopted being to refractionate each fraction two or three times, and then to treat each with mercuric chloride, a solution of the bases in hydrochloric acid being added to a hot 10 per cent. solution of mercuric chloride. It was generally found most convenient to use 2 mols. of mercuric chloride to one of base, as the salts obtained usually contain that amount of mercuric chloride, although occasionally more complex salts were found. The mercury salts were then recrystallised from water slightly acidified with hydrochloric acid until their melting points became tolerably constant and analysis showed them to be fairly pure. The base was next regenerated by removing the mercury either by caustic soda or by hydrogen sulphide, and if found to be impure the treatment with mercuric chloride repeated. There are very great discrepancies between the boiling points of the bases recorded by different observers, partly because of the difficulty of obtaining them in the pure condition, and partly because of the great influence of variations in the height of the barometer; we have determined all boiling points with "short scale" thermometers of very good quality, the column of mercury being completely immersed in the vapour.

The following bases have been isolated :

Pyridine .....	B. p. 115—116°.
2-Methylpyridine ( $\alpha$ -picoline).....	B. p. 129·5° (763 mm.)
2:6-Dimethylpyridine .....	B. p. 142·5° (760 mm.)
2:4-Dimethylpyridine .....	B. p. 159—159·5°.
2:5-Dimethylpyridine .....	B. p. 154—155°.
2:4:6-Trimethylpyridine .....	B. p. 170·5° (763 mm.)

### *Pyridins.*

Three attempts were made to isolate pyridine by Mohler's method of precipitation with a strong solution of potassium ferrocyanide (*Ber.*, 1888, 21, 1015), but without success, as the base recovered from the precipitate showed no constant boiling point, but distilled between

115° and 130°. Apparently this method may be advantageously used for freeing pyridine from small quantities of its homologues, but not for separating small quantities of the base from larger amounts of picoline, &c.

The base (about 10 grams) recovered from these experiments was therefore boiled with excess of potassium permanganate solution, and the liquid distilled; from the distillate, 3 grams of base boiling almost entirely between 115° and 116° were recovered; it gave a yellow, crystalline platinichloride melting at 228—230° without decomposition. On analysis:

0.2665 gave 0.0915 Pt. Pt = 34.33.

$(C_6H_5N)_2, H_2PtCl_6$  requires Pt = 34.33 per cent.

### *2-Methylpyridine ( $\alpha$ -Picoline).*

From the lower fractions was isolated a fair quantity of a mercuric compound of 2-methylpyridine crystallising in small plates melting at 151°:

0.6330 gave 0.4390 HgS. Hg = 59.79.

0.5490 „ 0.3800 HgS. Hg = 59.67.

$C_6H_7N, HCl, 2HgCl_2$  requires Hg = 59.61 per cent.

This salt yielded a base which was a colourless liquid, easily soluble in water, with a powerful pyridine-like odour, boiling at 129.5° under 763 mm. pressure. Its platinichloride formed orange-red crystals melting at 194° with decomposition, and on analysis gave 32.65 per cent. of platinum (calculated 32.72 per cent.). The base was oxidised by potassium permanganate, and after removal of manganese and potassium salts, treated with copper acetate, when it gave the beautiful violet-blue, crystalline copper salt characteristic of picolinic acid. From this copper salt, the acid was obtained; it crystallised from a mixture of alcohol and ether in thin, colourless needles melting at 134°.

### *2:4-Dimethylpyridine.*

This base was isolated from the fractions boiling between 150° and 165° by means of its mercurichloride, and is a colourless liquid, easily soluble in cold, but sparingly so in hot water; it has a characteristic cucumber-like odour; its sp. gr. at 14° is 0.9380 and it boils at 159—159.5°.

Its mercurichloride forms fine needles melting at 127°. On analysis:

0.4870 gave 0.3305 HgS. Hg = 58.49.

0.6390 „ 0.6662 AgCl. Cl = 25.77.

0.3622 „ 0.3796 AgCl. Cl = 25.90.

$C_7H_9N, HCl, 2HgCl_2$  requires Hg = 58.41; Cl = 25.84.

The picrate was obtained by direct precipitation as a yellow precipitate melting at 178—180°.

With auric chloride, the base gave a yellow oil which rapidly crystallised and melted at 94° without decomposition. On analysis :

0·4454 gave 0·1958 Au. Au = 43·95.

$C_7H_9N, HCl, AuCl_3$  requires Au = 44·13 per cent.

The platinichloride crystallises extremely well in orange-red crystals, which become dim on exposure to air without losing weight ; on slow heating, they melt at 216°, and on rapid heating at 223° with decomposition. On analysis :

0·3020 gave 0·0951 Pt and 0·4126 AgCl. Pt = 31·49 ; Cl = 33·78.

$(C_7H_9N)_2, H_2PtCl_6$  requires Pt = 31·24 ; Cl = 34·00 per cent.

On oxidation, an acid was obtained crystallising in white, silky needles containing water of crystallisation and melting at 235° with decomposition ; with ferrous sulphate, it gives a deep red colour ; with copper acetate, no precipitate even on boiling ; with silver nitrate, a white, flocculent precipitate ; and with lead acetate a white precipitate soluble in excess, the solution depositing crystals on standing.

When heated at 210° for two hours, the acid decomposed, giving a white sublimate and an infusible residue ; both the sublimate and the residue sublimed without melting when heated at above 200°, and were proved to be isonicotinic acid by this fact, and also by their behaviour with ferrous sulphate, silver nitrate, copper acetate, and lead acetate.

The acid is, therefore, lutidinic acid, and the base 2:4-dimethylpyridine.

#### 2:5-Dimethylpyridine.

This base (which had not previously been described) was isolated from the fractions boiling at 150—165° by means of its mercurichloride ; this salt forms small, heavy crystals melting at 163°, and contains 6 mols. of mercuric chloride. On analysis :

0·5260 gave 0·4120 HgS and 0·5472 AgCl. Hg = 67·51 ; Cl = 25·70.

0·5515 „ 0·4315 HgS „ 0·5746 AgCl. Hg = 67·42 ; Cl = 25·22.

0·9688 „ 1·0140 AgCl. Cl = 25·86.

$C_7H_9N, HCl, 6HgCl_2$  requires Hg = 67·43 ; Cl = 25·86 per cent.

The base is a colourless liquid boiling at 154—155° and gives a picrate melting at 151—152°.

The aurichloride melts at 156—157° without decomposition. On analysis :

0·1681 gave 0·0738 Au. Au = 43·90.

$C_7H_9N, HCl, AuCl_3$  requires Au = 44·13 per cent.



The *platinichloride* is of an orange-red colour and crystallises well, but very diverse melting points were observed with the same samples on different days, the lowest being  $195^{\circ}$  and the highest  $216^{\circ}$ ; the *anhydrous* salt melts at  $238^{\circ}$  with decomposition. On analysis:

0.8671 hydrated salt lost  $0.0472 \text{ H}_2\text{O}$  at  $105^{\circ}$ .  $\text{H}_2\text{O} = 5.44$ .  
 $(\text{C}_7\text{H}_5\text{N})_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 5.46$  per cent.  
 0.3169 anhydrous salt gave  $0.0970 \text{ Pt}$ .  $\text{Pt} = 30.62$ .  
 0.2291        ,,         $0.2290 \text{ CO}_2$  and  $0.9654 \text{ H}_2\text{O}$ .  $\text{C} = 27.14$ ;  $\text{H} = 3.17$ .  
 0.2502        ,,         $0.2457 \text{ CO}_2$    ,,    $0.0740 \text{ H}_2\text{O}$ .  $\text{C} = 26.79$ ;  $\text{H} = 3.36$ .  
 $(\text{C}_7\text{H}_5\text{N})_2, \text{H}_2\text{PtCl}_6$  requires  $\text{C} = 26.93$ ;  $\text{H} = 3.21$ ;  $\text{Pt} = 31.24$  per cent.

On oxidation, an acid melting at  $237\text{--}238^{\circ}$ , with effervescence was obtained. With ferrous sulphate, it gave a fine yellow colour; with copper acetate, a bright blue precipitate on boiling; with silver nitrate, a white, gelatinous precipitate, and with lead acetate, a white precipitate insoluble in excess. On treatment with methyl alcohol and hydrochloric acid, it formed an ester crystallising in white needles melting at  $160^{\circ}$ .

When heated for 2 hours at  $210^{\circ}$ , it decomposed, and the residue sublimed completely; that this residue was nicotinic acid was proved by its melting at  $229^{\circ}$  and by its behaviour with copper acetate, ferrous sulphate, and silver nitrate.

The acid is therefore *isocinchomeronic* acid, and the base 2:5-dimethylpyridine.

Since the above was completed, Errera (*Ber.*, 1901, 34, 3699) has obtained this base synthetically, but in too small quantity for purification, and his description in no way agrees with ours, possibly because his compound had not been thoroughly purified.

### 2:6-Dimethylpyridine.

From the fraction boiling between  $140^{\circ}$  and  $145^{\circ}$ , a considerable quantity of the trimercuric salt of this base was obtained in colourless plates melting at  $160\text{--}161^{\circ}$ . On analysis:

0.6725 gave  $0.4900 \text{ HgS}$ .  $\text{Hg} = 62.80$ .  
 0.5395   ,,     $0.3935 \text{ HgS}$ .  $\text{Hg} = 62.86$ .  
 $\text{C}_7\text{H}_5\text{N}, \text{HCl}, 3\text{HgCl}_2$  requires  $\text{Hg} = 62.77$ .

A second mercurichloride of this base was obtained from several of the fractions of low boiling point, and forms small, lustrous scales resembling cadmium iodide; it melts at  $186^{\circ}$ . On analysis:

0.5034 gave  $0.2817 \text{ HgS}$ .  $\text{Hg} = 48.32$ .  
 $\text{C}_7\text{H}_5\text{N}, \text{HCl}, \text{HgCl}_2$  requires  $\text{Hg} = 48.30$  per cent.

The base itself was found to be a colourless liquid, fairly easily

soluble in water, having a characteristic odour resembling that of both pyridine and peppermint, and boiled at  $142.5^{\circ}$  under 760 mm. pressure.

The platinichloride crystallised well and melted at  $210^{\circ}$  with decomposition. On analysis :

0.422 gave 0.3175 Pt. Pt = 31.22.

$(C_7H_9N)_2, H_2PtCl_6$  requires Pt = 31.24 per cent.

The base was oxidised by potassium permanganate, and gave a good yield of *dipicolinic acid* (Ladenburg, *Ber.*, 1885, 18, 53, and Epstein, *Annalen*, 1885, 231, 1). After filtering off the precipitated oxide of manganese, the solution was reduced to a small bulk, acidified slightly with dilute sulphuric acid, and left to stand for some hours, when a crystalline precipitate (apparently a mixture of the free acid and an acid potassium salt) was obtained. This was warmed up with absolute alcohol and a little hydrochloric acid, and some potassium chloride filtered off; from the filtrate the acid separated in rosettes of needles melting at  $232^{\circ}$ , and these, on recrystallising from alcohol, formed very small prisms melting at  $226^{\circ}$  (darkening at  $225^{\circ}$ ), whilst from water they gave long, hair-like crystals also darkening at  $225^{\circ}$  and melting at  $226^{\circ}$ . Further recrystallisation produced no change in the melting point, and on no occasion were we able to confirm Epstein's observation of  $236^{\circ}$  as the melting point of this acid.

#### 2 : 4 : 6-Trimethylpyridine (*s*-Collidine).

From several fractions between  $150^{\circ}$  and  $180^{\circ}$ , considerable quantities of a mercuric compound were obtained which separated in large, fern-like or saw-like crystals built up apparently of many small plates, and melted at  $154^{\circ}$ . The mean of four determinations gave 57.16 per cent. of mercury (maximum 57.3, minimum 56.97 per cent.), the percentage calculated for  $C_8H_{11}N, HCl, 2HgCl_2$  being 57.22.

From 200 grams of this salt, 25 grams of base were recovered and again worked up with mercuric chloride; the salt formed after being fractionally crystallised yielded 93 grams of crystals melting sharply at  $154^{\circ}$  and yielding 13 grams of the base :

0.483 gave 0.3215 HgS. Hg = 57.38 per cent.

The base was a colourless liquid with a not unpleasant odour; its sp. gr. at  $20^{\circ}$  was 0.917, and it boiled at  $170.5^{\circ}$  under 763 mm. or at  $169.5$ — $170^{\circ}$  under 746 mm. pressure. Its platinichloride was easily obtained in well defined, orange-red crystals melting at  $223$ — $224^{\circ}$  with decomposition.

On oxidation, an acid crystallising in feathery needles, darkening at  $225^{\circ}$  and melting at  $228^{\circ}$ , was obtained; and this yielded, with abso-

lute alcohol, an ester melting at  $127.5^{\circ}$ . It is therefore trimesitic acid, and the base must be the 2 : 4 : 6-trimethylpyridine.

The authors have pleasure in stating that this work has been carried out by the aid of a grant from the Research Fund Committee of the Chemical Society.

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# XLVI.—*The Transport Number of very Dilute Solutions.*

By B. D. STEELE, B.Sc., and R. B. DENISON, B.Sc. (1851 Exhibition Scholars).

IN discussing the constitution of certain salt solutions, it was recently shown by one of us (Steele, *Phil. Trans.*, 1902, 198, A, 105) that if the change in transport number which undoubtedly occurs with change in concentration for salts such as magnesium chloride, is assigned to a variation of the specific velocity of the chlorine and magnesium ions into which the salt is assumed to be ionised; and that if  $u$  and  $v$  represent the specific velocities of cation and anion at a given concentration  $n$ , and if  $u_1$  and  $v_1$  represent the values of the velocities of the same ions at the concentration  $n_1$ , a similar relation to the following holds for a large number of salts.

In the case of calcium chloride, between  $n=0.01$  and  $n=5.0$  the anion transport number  $p$  varies between 0.58 and 0.74. In the dilute solution,  $u = \frac{42}{58}v = 0.723v$ , and in the stronger solution  $u_1 = \frac{26}{74}v_1 = 0.350v_1$ , and hence  $\frac{u}{u_1} = 2.06 \frac{v}{v_1}$ , or, assuming the velocity of the anion to remain constant, that of the cation has diminished by more than one-half.

It was also shown that, if the coefficient of ionisation is given even approximately by the relation  $\alpha = \frac{\mu}{\mu_{\infty}}$ , where  $\mu$  is the molecular conductivity at the given concentration and  $\mu_{\infty}$  that at infinite dilution, then we get the astonishing result that, as the concentration of the calcium chloride increases, the velocity of the Ca ion is steadily diminished, whilst that of the Cl ion is correspondingly increased.

A far more satisfactory explanation of the change in question is that first suggested by Hittorf, who assumed the existence of complex ions

in such salt solutions; a solution of magnesium chloride of which the anion transport number is found to increase with increasing concentration would, according to this conception, consist of a certain proportion of simple chlorine and magnesium ions, and in addition to these a certain number of complex anions; and since the proportion of the latter increases with concentration, the transport number would, as in the case of cadmium chloride, be greater than unity, provided sufficiently concentrated solutions could be investigated (Hittorf, *Pogg. Annalen*, 1859, 106, 546).

For a solution containing complex anions of one species only in addition to the simple ions, if  $u$ ,  $v$ , and  $v'$  are the specific velocities of the cation, anion, and complex anion respectively, and if  $c$  is the ionic concentration of the cation,  $c'$  that of the complex anion, then  $c - c'$  is the concentration of the simple anion, and the expression for the anion transport number is

$$p = \frac{(c - c')v + c'v'}{cu + (c - c')v + c'v'} = \frac{cv + c'(v' - v)}{c(u + v) + c'(v' - v)} \quad (1)$$

In determining  $p$  experimentally by Hittorf's method, the quantity represented by the denominator is correctly measured by means of a silver voltameter; the numerator, on the other hand, is determined as a concentration change brought about by the migration of the ions, and hence the degree of complexity of the complex anion has to be taken into consideration. If  $m$  is the number of monad anions into which the complex would ionise if completely dissociated, then the increase in concentration at the anode is proportional to  $(c - c')v + c'mv'$ , and the above becomes

$$p = \frac{cv + c'(mv' - v)}{c(u + v) + c'(v' - v)} = \frac{v + \alpha(mv' - v)}{u + v + \alpha(v' - v)} \quad (2),$$

where  $\alpha = \frac{c'}{c}$ , or the ratio of complex to total anions. If this expression is put into the form

$$p = \frac{v + \alpha(v' - v) + \alpha v'(m - 1)}{v + \alpha(v' - v) + u},$$

it is seen at once that in order that  $p$  should be  $> 1$ , it is only necessary that  $\alpha v'(m - 1)$  should be greater than  $u$ , a relation which is fulfilled if either  $\alpha$  or  $m$  is large. For the majority of salts, neither of these factors attains a sufficient magnitude; but for zinc chloride and cadmium chloride,  $p$  is greater than 1 for very concentrated solutions, and the presence of complex anions in solutions of these salts is universally recognised.

Equation 2 shows at once that no constant value for  $p$  can be

obtained in solutions of a salt which forms complex ions, since  $\alpha$  would vary with the concentration; for such salts, it is only at dilutions at which  $\alpha$  disappears that the equation takes the form

$$\text{given by Hittorf, } p = \frac{v}{u+v}.$$

Since the value for the specific ionic velocity, which is given by the relation  $v = p\mu_{\infty}$  and  $u = (1-p)\mu_{\infty}$ , depends on the correctness of Hittorf's equation, it is obvious that, in the case of ions which show a tendency towards the formation of complexes, a constant value for  $u$  or  $v$  can only be obtained when  $p$  is determined for solutions of such dilution that no complexes exist; for more concentrated solutions,  $p\mu_{\infty} = v + x$  and  $(1-p)\mu_{\infty} = u - x_1$  if the change is an increase of  $p$  with concentration, and *vice versa*.

If, however,  $p$  can be measured in sufficiently dilute solutions of several salts containing a common ion, then the value for the specific ionic velocity of the latter should be the same, whatever the salt from the measurements of which it is calculated. The problem is, in fact, the determination of the transport number at increasing dilutions until it is found to remain constant.

For the calculation of  $u$  and  $v$ , it is therefore necessary that we should know both the molecular conductivity at infinite dilution and the "constant" transport number. The former of these is obviously not capable of direct experimental determination; but from measurements at very great dilutions, which have been carried out by Kohlrausch and others, it can be correctly obtained by extrapolation.

The transport number, on the other hand, if we leave out of consideration salts of the type of potassium chloride and nitrate, for which it is practically constant at all concentrations, has not yet been systematically determined at what may be called "constant" dilutions. To the large class of salts, for which, at ordinary concentrations, considerable variations in  $p$  are found to take place, belong all salts of dyad and triad ions, and for only a few of these has the "constant" range of concentration been reached. This is due to the fact that the determination of  $p$  for very dilute solutions is, for several reasons, a matter of the greatest difficulty.

In all Hittorfian transport number determinations, it is necessary that a certain portion of the solution between the electrodes should remain unchanged in concentration. In the earliest of these determinations, in order that this might be the case, an experiment could only be carried on for a very limited time, as otherwise, by the migration of the H and OH ions developed at the electrodes, concentration changes took place through the whole column of liquid. This difficulty has been overcome in various ways, the method employed by Hittorf

being the use of a cadmium anode to prevent the formation of H ions ; and to prevent the development of OH ions, the cathode was surrounded with a concentrated acid solution.

Hopfgartner (*Zeit. physikal. Chem.*, 1898, 25, 115) employed a zinc anode, and at the cathode a concentrated solution of zinc chloride over a mercury cathode.

A further source of error is that due to mixing by diffusion, on account of the large concentration changes that take place during electrolysis in the neighbourhood of the electrodes. This has been eliminated quite recently by Noyes (*Zeit. physikal. Chem.*, 1901, 36, 63), who adds to the cathode and anode solutions respectively in a W-shaped apparatus, solutions of the acid and alkali of which the original salt was composed, and of such a strength that the concentration of the salt at the electrodes remains unaltered. By this means, extremely accurate results were obtained by Noyes, but unfortunately the method cannot conveniently be applied to extremely dilute solutions.

The only measurements of such solutions which have been made, until quite recently, are those of Bein (*Zeit. physikal. Chem.*, 1898, 27, 1). In all his experiments, however, the amount of matter which was transported did not exceed 9—30 milligrams of chlorine, this being determined as the difference between two very much larger quantities of material. Accurate measurements of dilute solutions have recently been made by Jahn's pupils (*Zeit. physikal. Chem.*, 1901, 37, 674); the method employed was one in which the development of H and OH ions was prevented by the use of a cadmium anode and a mercury cathode covered by a concentrated solution of copper salt. A very high voltage was employed, and, in the analytical work, the limit of possible accuracy was approached ; in some of the experiments, a very large concentration change at the electrodes took place, apparently without affecting the concentration of the intermediate portion. The method is, however, not applicable for solutions more dilute than about  $N/150$ .

Jahn criticises the employment of any method which results in the development of gas bubbles at the electrodes, remarking that this gives rise to quite uncontrollable currents, which cause the whole solution to become mixed. Noyes, on the other hand, obtained perfectly concordant results by the use of a properly shaped apparatus, and blank experiments have been carried out by the authors, which will be described immediately, and which show that in an apparatus of the shape of that used by Noyes, absolutely no disturbance of the intermediate portion takes place by the gas development at the electrodes even after 48 hours.

It is worth pointing out that the only salt the transport number

of which has been determined by both Noyes and Jahn is barium chloride, and for this salt the following values were found for  $p$ .

$N/50$   $p = 55.69, 55.81, \text{ and } 55.84$ . Mean = 55.78 (Noyes).

$N/60$   $p = 54.2, 54.4, \text{ and } 54.3$ . Mean = 54.3 (Jahn).

These two values differ by about 3 per cent., or about ten times as much as the extreme error in either series. From the fact that by Noyes' method no concentration changes occur during an experiment, his figures should, perhaps, be of the greater value.

The object of the experiments that have been undertaken was two-fold; firstly, to develop a general method by means of which it would be possible to determine the transport number at dilutions comparable with those at which accurate conductivity measurements are made; and secondly, to test the question as to whether, from the results so obtained, constant values for the migration constant of such an ion as  $\text{Ca}^{++}$  would be found. The salts of calcium were selected for the experiments, because good measurements of their conductivities have been made at dilutions down to  $n = 0.0001$ .

The concentration of the solutions that have been measured varies between  $n = 0.00529$  and  $n = 0.0025$ .

It is probably not practicable to work at dilutions greater than the latter on account of the conductivity of ordinarily purified distilled water and the practical impossibility of rigorously purifying such large quantities as are required for the experiments.

In solutions containing so small an amount of salt as those under consideration, it is obvious that, in order to get any considerable quantity of salt carried by the current, it is necessary, either to electrolyse a very large volume of solution, or, using smaller volumes, to carry the experiment for so long a time that a very large change in concentration is brought about. If the usual method is employed, the former of these alternatives requires the use of an apparatus of unmanageable size, whilst the latter is attended with the danger of loss of the experiment on account of the backward diffusion and consequent change in concentration of the middle portion.

The apparatus, shown in Fig. 1 (p. 461), admits of the possibility of electrolysing an unlimited volume of liquid in a vessel of reasonable size.

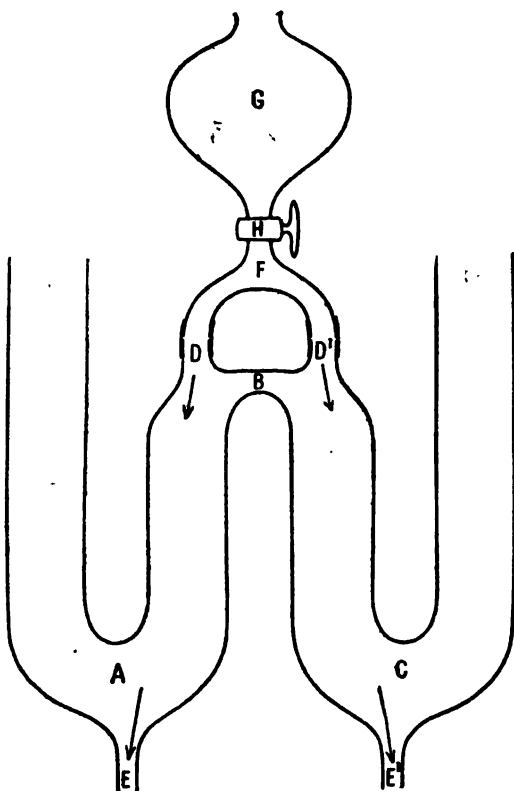
The electrolysing vessel consists of two U-tubes,  $A$  and  $C$ , of about 4.0 cm. diameter, one limb of each being bent away at right angles, and the two sealed together at  $B$ ; two narrow glass tubes are sealed in at  $E$  and  $E'$ , and two wider ones at  $D$  and  $D'$ , the total length from  $D$  to  $E$  being about 25 cm.  $D$  and  $D'$  are connected by means of rubber tubing to the T-piece,  $F$ , which in its turn is joined to the large stoppered funnel  $G$ ; the small tubes,  $E$  and  $E'$ , are each connected with pieces of long, narrow bore glass tubing which can be brought out

over the edge of the thermostat, these are closed either by stopcocks or by rubber tubes and pinchcocks. The U-tubes, *A* and *C*, are each supplied with an electrode vessel which is shown in Fig. 2 (p. 462). This consists of the cup *c*, about 4 cm. in height and 2.0 cm. in diameter, which is attached to the bent up piece of the broad capillary tube *a*, the end of which passes through and projects for about 2 cm. into the cup *c*; the other end of the tube *a*, after passing through the cork, *g*, is sealed to the bulb *b*, and is provided with a stopcock *h*; through the cork *g*, passes also the short tube with stopcock *d*, and the glass tube *f*, to which is attached the platinum electrode, *e*, which surrounds the projecting piece of tubing. The cork *g* is hermetically sealed with sealing wax into the open end of the tube *A* (Fig. 1).

To prevent the formation of  $H$  and  $OH$  ions at the anode and cathode respectively, solutions of alkali and acid are added. Working with such dilute solutions, it was not found convenient to add solutions of sufficient dilution to counter-

balance the concentration changes, as was done by Noyes, on account of the very large volumes of such solutions that would be required; small quantities of half normal solutions were therefore used instead. The experiment is carried out in the following manner. The apparatus is first placed in position in a large water-bath, and the two tubes attached to *E* and *E'* are brought out over the edge. All the stopcocks are then closed. *G* is next filled with

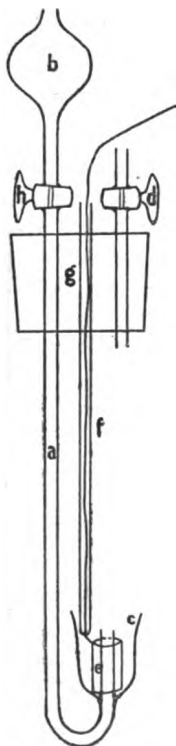
FIG. 1.





the solution to be electrolysed, and this is allowed to run into the apparatus, more solution being added to *G* as required. When the last bubbles of air in *F* have been got rid of (by suction if necessary), the stopcocks, *d*, are cautiously opened, and the liquid allowed to rise in the outer limbs of *A* and *C* to a point about 2 or 3 cm. above the electrode vessel, *c*. The stopcocks, *d*, are then closed. The solutions of acid and alkali are next added. If the solution of both electrodes is to be subsequently analysed, it is necessary to know exactly

FIG. 2.



the quantity of each solution which is added; in all the experiments tabulated, the cathode solution only was analysed, and therefore the acid only was weighed. This was done by means of a glass weighing pipette of about 30 c.c. capacity, which was weighed before and after each experiment. After weighing the pipette, about 1 c.c. of the acid is transferred to the bulb *b*; all the stopcocks but *d* being closed, the acid is allowed to run in slowly by carefully opening the stopcock *h*; the acid runs in through the tube *a*, and since its density is very much greater than that of the solution, falls over and around the electrode *c* and lies at the bottom of the cup *c*. A similar quantity of alkali is added in the same manner to the anode. In order to judge when the reagent becomes exhausted, small quantities of an indicator are added simultaneously. In the majority of cases, methyl-orange was the indicator employed. From time to time during the experiment, fresh quantities of acid and alkali are added in the same manner when they are shown to be required by the reaction of the indicator. The electrodes are connected with the terminals of the battery, a silver voltameter whose platinum cathode had an area of about 1 sq. cm. being placed in circuit, and the experiment is started by inserting the cathode. Under ordinary

circumstances, an experiment arranged in this manner could not be allowed to run more than 60 to 80 minutes with a voltage of 60 volts without concentration changes reaching the portion *B*; but in that time very small quantities of salt will have been transported. About every twenty minutes the portion of solution contained in the inner limb of the U-tube is removed as follows. To remove the portion from *A*, all the stopcocks being closed, *H* is first opened, and then very carefully the stopcock attached to *E*; the solu-

tion then flows in the direction of the arrows marked (1), and is collected in a suitable vessel and weighed; on now closing  $E$  and opening  $E'$  the current flows in the directions indicated by the arrows (2), and the solution from  $C$  is thus removed. Unless it is desired to analyse this portion also it is not collected, but is allowed to run off.

The duration of experiments varied according to the voltage used from 7 to 36 hours; in the later ones, with a voltage of 170 to 180, 7 to 8 hours was usually sufficient, but with the earlier ones, using 70 volts only, the experiment was allowed to run overnight with a low voltage, to prevent danger of mixing in  $B$ . To test the question as to whether mixing occurs due to gas development at the electrodes, the apparatus was arranged as described, a small quantity of phenolphthalein being added to the whole volume of solution. No liquid was removed, but the circuit was closed for short periods every half-hour or so, so as to start the convection currents in the outer limbs of the apparatus. After a lapse of 48 hours, no trace of alkali could be detected as having found its way into the portion  $B$  of the apparatus. A similar experiment with litmus failed to detect either acid or alkali at  $B$ .

After the three salts of calcium had been measured, the method as above described was slightly modified, with the result that subsequent experiments with potassium chloride gave much more closely agreeing figures. This is probably due partly to the fact that the modification eliminates certain very small sources of error, and partly also to the fact that chlorine is capable of far more accurate determination as silver chloride than calcium as calcium sulphate. The modification consists in the attachment of long capillary tubes to  $E$  and  $E'$ , so that, instead of periodically removing the solution, it is allowed to flow through the apparatus in a steady but very slow stream during the whole course of the experiment. At the conclusion of an experiment, all the stopcocks are closed, and the current is disconnected by removing the cathode from the silver voltameter; the cathode is immediately washed in distilled water and dried with alcohol. The T-piece,  $F$ , is then disconnected from the tubes,  $D$  and  $D'$ , and the solution from  $B$ , and to a depth of about 4 cm. in  $A$ , is removed through  $D$  by means of a large pipette; this portion is weighed for analysis, as the middle portion. On opening now the stopcock attached to  $E'$ , the solution from  $C$  is run out. The apparatus is then lifted from the water-bath, and the remaining solution from the cathode limb,  $A$ , is removed through  $E$ , and finally the whole of this limb, the bulb,  $b$ , and the cup,  $c$ , rinsed out several times with small quantities of the original solution, all the rinsings being added to the cathode solution for analysis. If it is required to analyse the solution from the anode, the limb,  $C$ , must of course be treated in the same manner.

For analysis, the solutions were in all cases evaporated to a small bulk; this was done as each portion of liquid was removed from the apparatus.

The calcium salts were in all cases estimated as sulphate; in the case of the chloride and nitrate, the solution was evaporated over a water-bath in a large porcelain evaporating basin, the evaporation being continued until the solution to be analysed, which varied between 2 and 3 litres, was reduced to about 100 c.c.; it was then transferred to an accurately weighed platinum basin of about 250 c.c. capacity, a very slight excess of sulphuric acid was added, and the solution evaporated to dryness on the water-bath, the basin being finally ignited at a dull red heat.

In the earlier experiments, the basin was covered during ignition with a piece of ashless filter paper, which was afterwards burnt, and the ash weighed separately, but as in no case was a weighable quantity of ash so obtained, the basin, in subsequent experiments, was simply covered during ignition with a clean clock-glass.

The analysis of the calcium sulphate solution could not be carried out in the same manner on account of the separation of the calcium sulphate, and the impossibility of transferring this without loss from the porcelain to the platinum basin. It was therefore necessary to evaporate in a vessel which could be afterwards weighed.

The evaporation of 3 litres of solution in a basin of 250 c.c. capacity was an operation too slow to be attempted; a large platinum basin holding about half a litre, and weighing 300 grams, was therefore employed, and the solution after weighing was transferred directly to this, and the solid calcium sulphate weighed in it. The difficulty of performing analytical operations of great accuracy under these conditions probably accounts for the greater variations found for the transport number of calcium in calcium sulphate.

In the experiments with potassium chloride, the chlorine was estimated as silver chloride, the solution being, as before, evaporated to a comparatively small bulk, usually about 150 c.c.\*

The precipitate was collected in a Gooch crucible and weighed, after thorough washing and drying, at a temperature of 180°. An attempt was made to estimate the potassium chloride by direct evaporation and weighing the residue, but this led in all cases to results far too low, pointing either to volatilisation of the salt in steam from concentrated solutions, or, what seems more probable, to loss from

\* If it is desired, as in transport number determinations, to estimate the chlorine to the nearest tenth of a milligram, this concentration is necessary; for, since the solubility of silver chloride in water at 18° amounts to 1.5 mg., corresponding to 0.4 mg. chlorine per litre, the estimation in very large volumes of dilute solutions is attended with a constant error of considerable magnitude.

spiriting, even when no higher temperature than that of a water-bath is employed.

The calculation of the results will be best rendered clear by the following example, that of calcium nitrate. In this experiment, these were passed through the cathode limb of the apparatus, weighed, and evaporated, 2702·94 grams of solution, including 26·20 grams of nitric acid, added to the electrode during electrolysis. Deducting the latter, the weight of solution analysed was 2676·74 grams, which before the experiment would yield 0·8932 gram of calcium sulphate. On analysis afterwards, it was actually found to yield 1·0205 grams of calcium sulphate.

The difference, 0·1273 gram, gives the actual amount of calcium, calculated as sulphate, which had been brought to the cathode by the current. During the experiment, 0·4517 gram of silver had been deposited on the cathode of the voltameter; if 108 is the atomic weight of silver, and 68 the equivalent weight of calcium sulphate, the expression  $\frac{0\cdot1273 \times 108}{68 \times 0\cdot4517} = 1 - p$  gives at once the transport number of the calcium ion in  $\text{CaSO}_4$ . In making the calculation for more concentrated solutions, a further correction is required for the volume changes brought about by the movement of the ions during electrolysis; but at the dilutions dealt with in the present paper this correction is quite negligible.

In the table are given the values found for the transport numbers, and also the data from which these are calculated; in the first column are given under *N* the concentration of the solutions in gram equivalents per litre; the second column gives the weight of the solution analysed, these are the actual weights of solution removed from the cathode less the weight of acid added during the experiment. The next two columns give the salt contents of this quantity of liquid, under "original" being tabulated the contents calculated from analyses made on the original solution, and under "final" the actual weight of salt found to be present after electrolysis. The difference between these is given in the next column as salt transported. In the case of the calcium salts, all the figures refer to calcium sulphate found on analysis, reduction to weight of calcium nitrate and chloride for these salts being unnecessary. In the case of potassium chloride, all the figures refer to the weight of silver as calculated from the silver chloride weighed. In the seventh, eighth, and ninth columns are tabulated the results of the analyses of the middle portion for the various experiments; three of these were unfortunately lost.

A comparison of the results given above with those obtained by previous investigators cannot be made for calcium sulphate and nitrate. For calcium chloride, values for the transport numbers have been found

by Hittorf, Bein, and others, which are gathered together and tabulated by Kohlrausch as follows :

$N =$	10	5	2	1	0.2	0.05	0.02	0.01
$1 - p =$	0.21	0.263	0.30	0.314	0.34	0.39	0.41	0.42

which approach with diminishing concentration the value found by us for  $N = 0.004$ .

Our value for potassium chloride is in agreement with all the best determinations, and is confirmatory of Kohlrausch's fundamental assumption as to the constancy of the transport number for this class of salt with increasing dilution.

### *The Specific Ionic Velocities.*

From the figures given above, it is possible to calculate, by the aid of the conductivity, the migration constants of the ions  $\frac{1}{2}\text{Ca}$ ,  $\text{K}$ ,  $\frac{1}{2}\text{SO}_4$ ,  $\text{Cl}$ , and  $\text{NO}_3$ ; the results so obtained are grouped together in the following table :

Salt.	$\mu_{\infty}$ .	$1 - p$ .	Ion.	$u$ .	$v$ .
$\text{CaSO}_4$ .....	122.0	0.441	$\frac{1}{2}\text{Ca}$	53.8	
			$\frac{1}{2}\text{SO}_4$		68.2
$\text{Ca}(\text{NO}_3)_2$ .....	115.5	0.450	$\frac{1}{2}\text{Ca}$	52.0	
			$\text{NO}_3$		63.5
$\text{CaCl}_2$ .....	118.7	0.438	$\frac{1}{2}\text{Ca}$	52.0	
			$\text{Cl}$		66.7
$\text{KCl}$ .....	131.5	0.495	$\text{K}$	65.1	
			$\text{Cl}$		66.4

To which may be added, for purposes of comparison and discussion, Noyes' figures for  $\text{K}_2\text{SO}_4$  :

$\text{K}_2\text{SO}_4$ .....	135.5	0.496	$\text{K}$	67.2	
			$\frac{1}{2}\text{SO}_4$		68.3

Of the above, the figures for  $\text{K}$  and  $\text{Cl}$  from  $\text{KCl}$  merely confirm the accepted values. It is further seen at once, by a comparison of the figures for  $\text{Cl}$  from calcium and potassium chlorides, that, at the dilutions at which  $p$  has been determined for these salts, calcium chloride dissociates in such a manner as to form chlorine ions having the same velocity as those formed by the dissociation of potassium chloride; the dissociation at these dilutions is therefore normal. Looking next at the velocity of the calcium ion, this is seen to be identical for solutions of the nitrate and chloride; very dilute solutions of these salts seem therefore strictly to obey the law of the independent wandering of the ions and to be comparable with potassium chloride in more concentrated solutions. If, however, these two salts are



N.	Solution from cathode.				Silver deposited in voltameter.	Middle portion.				Cation transport number.	Mean.	
	Weight of solution.	Salt contents.		Salt transported.		Weight of solution.	Salt contents.		Original.			Final.
		Original.	Final.				Original.	Final.				
0.00529	2279.24	0.8211	0.9408	0.1197	0.4402	231.24	0.0831	0.0835	0.432	0.438		
0.00421	2370.44	0.6783	0.7991	0.1209	0.4316	224.61	0.0643	0.0641	0.445			
0.00419	2470.39	0.7029	0.8226	0.1197	0.4342	228.94	0.0652	0.0660	0.438			
<i>Calcium chloride, CaCl<sub>2</sub>.</i>												
0.0025	3084.0	0.83320	0.70859	0.12461	0.2452	168.61	0.04502	0.04553	0.491	0.495		
0.0025	2992.0	0.84625	0.48554	0.16071	0.3161	178.6	0.04768	0.04825	0.492			
0.0046	2541.3	1.26030	1.00689	0.25341	0.5019	183.27	0.09089	0.09080	0.495			
0.0037	2398.9	0.96748	0.81809	0.14939	0.2984	170.50	0.06876	0.06880	0.499			
0.0034	3157.9	1.15263	0.98489	0.16774	0.3842	173.13	0.06318	0.06353	0.498			
0.0041	2737.4	1.20884	1.03865	0.17019	0.3377	174.3	0.07697	0.07708	0.496			
0.0086	2229.5	0.85315	0.67477	0.17838	0.3522	—	—	—	0.494			
0.0086	3164.0	1.21075	0.98475	0.22600	0.4473	214.2	0.08213	0.08197	0.495			
0.0027	2915.5	0.85162	0.70021	0.15141	0.3009	206.0	0.08017	0.08067	0.497			
<i>Potassium chloride, KCl.</i>												

considered in less dilute solutions, entirely different values are obtained for  $u$  and  $v$ ; thus, for  $N/50$  calcium chloride,  $1-p=0.41$ , and accordingly,  $u=487$  and  $v=700$ .

The complex present in this solution is therefore one which diminishes the apparent cation velocity and increases the apparent anion velocity, since, by the dissociation of the complex, the latter cannot presumably be diminished below the value it has in salts such as potassium and sodium chloride. The dissociation of the complexes in calcium chloride, and also in the nitrate, appears to be complete.

The value for  $u$ , calculated from calcium sulphate, however, is found to be 3.46 per cent. higher than in either of the other salts. This behaviour would appear to be in some way connected with the presence of the sulphate ion, for the value for  $K$ , calculated from the potassium sulphate figures, is also higher than that calculated from the chloride or the nitrate, and, as a coincidence, it may be noted that the percentage increase is about the same; further, the value of  $v$  for  $SO_4$ , obtained from the potassium and the calcium salts, is practically identical.

It is conceivable that this may be due to a very small amount of hydrolysis occurring in very dilute solutions of sulphates, which at very great dilutions becomes of sufficient magnitude to give too high values for the molecular conductivity, and thus increase both  $u$  and  $v$ . It is certainly difficult to see how otherwise such enhanced values can be obtained.

It is our pleasant duty to express our thanks and indebtedness to Professor Abegg for his kindness and assistance to us during the course of our work.

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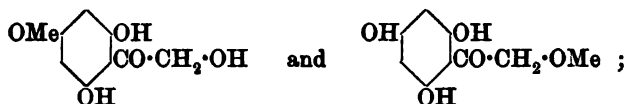
## XLVII.—*Rhamnazin and Rhamnetin.*

By ARTHUR GEORGE PERKIN, F.R.S.E., and JOHN RAYMOND ALLISON, B.Sc.

ALTHOUGH rhamnetin has been shown to be a monomethyl ether of quercetin (Herzig, *Monatsh.*, 1888, 9, 548), the locality of the methoxyl group has hitherto not been definitely ascertained, and either the (3) or the 7-position might equally well be assigned to it. Similarly, in rhamnazin (*Trans.*, 1897, 71, 818), a quercetin dimethyl ether although the position of one methoxyl group is known, that of the



second, as in the case of rhamnetin, is uncertain. Thus if rhamnetin or rhamnazin be decomposed by digestion with boiling alcoholic potash or by the aspiration of air through its alkaline solution, protocatechuic acid and vanillic acid respectively are produced besides a syrupy phloroglucinol derivative; the yield of the latter, however, is small, and being readily soluble it is difficult to identify; moreover, preparation of the raw material, especially rhamnazin, is extremely laborious. For the phenols in question, three constitutions were possible, namely, that of phloroglucinol monomethyl ether, or those of the hydroxyfisetol monomethyl ethers,



these two being suggested by Herzig's (*Monatsh.*, 1891, 12, 187) decomposition of fisetin tetramethyl ether into fisetol and veratric acid.

The study of the azobenzene derivatives of phloroglucinol (*Trans.*, 1897, 71, 189, 1154) and other compounds derived from it, has shown that such substances are sparingly soluble and readily crystallised, and it appeared likely that the phenols from rhamnetin and rhamnazin might be identified by these means.

*Rhamnazin* was decomposed by digestion for several days with boiling alcoholic potash, but this is more rapidly accomplished (in about two hours) by the aspiration of air through its solution in dilute aqueous potassium hydroxide. The phenolic product of the reaction which is the same in both cases, was isolated in the usual manner, and its solution in dilute sodium carbonate treated with diazobenzene sulphate until a precipitate no longer formed; this, which is orange-red, was collected, well washed, transferred to a dish, and dried on the water-bath. Extraction with alcohol removed a resinous compound, and the residue, after being crystallised two or three times from a mixture of alcohol and acetic acid, gave an average yield of about ten per cent. of the rhamnazin employed :

0.0919 gave 0.2208  $\text{CO}_2$  and 0.0377  $\text{H}_2\text{O}$ .  $\text{C} = 65.51$ ;  $\text{H} = 4.54$ .

0.0844 „ 11.7 c.c. nitrogen at  $16^\circ$  and 754 mm.  $\text{N} = 16.02$ .

$(\text{C}_6\text{H}_5\text{N}_3)_2\text{C}_6\text{H}_3\text{O}_2\cdot\text{OCH}_3$  requires  $\text{C} = 65.51$ ;  $\text{H} = 4.59$ ;  $\text{N} = 16.09$  per cent.

It formed glistening orange-red needles sparingly soluble in alcohol and melting at  $250\text{--}252^\circ$ .

*Rhamnetin* was decomposed by the same methods, and the phenolic product converted into its disazobenzene derivative. This melted at  $250\text{--}252^\circ$ , and was identical with that obtained from rhamnazin :

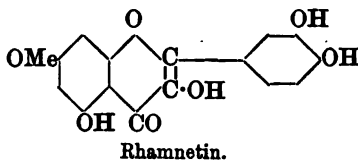
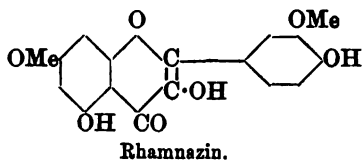
0.1136 gave 0.2715  $\text{CO}_2$  and 0.0475  $\text{H}_2\text{O}$ .  $\text{C} = 65.17$ ;  $\text{H} = 4.64$ .

0.1157 „ 15.6 c.c. nitrogen at  $14^\circ$  and 746 mm.  $\text{N} = 15.57$ .

0.1788 „ 0.1234 AgI.  $\text{OCH}_3 = 4.40$ .

$\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_4 \cdot \text{OCH}_3$  requires  $\text{C} = 65.51$ ;  $\text{H} = 4.59$ ;  $\text{N} = 16.09$ ;  $\text{OCH}_3 = 4.31$  per cent.

This compound is therefore *disazobenzene phloroglucinol monomethyl ether*, and the phenol obtained both from rhamnazin and from rhamnetin is phloroglucinol monomethyl ether. The relationship of these colouring matters may, therefore, be indicated by the formulæ,



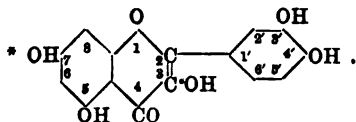
and the suggestion (*loc. cit.*) that rhamnazin was rhamnetin monomethyl ether is thus shown to be correct.

The shades given by these colouring matters upon mordanted wool are as follows:

	Chromium.	Aluminium.	Tin.	Iron.
Rhamnetin .....	Red-brown.	Brown-orange.	Bright orange.	Olive-black.
Rhamnazin .....	Golden-yellow.	Orange-yellow.	Lemon-yellow.	Olive-brown.

These results show that the dyeing properties of rhamnetin are identical with those of quercetin, and are interesting in that they prove that in quercetin the hydroxyl (7) \* has no effect on its dyeing properties. On the other hand, the replacement of the hydroxyl (3') by methoxyl with production of rhamnazin (compare also isorhamnetin, quercetin monomethyl ether [ $\text{OMe} = 3'$ ] *Trans.*, 1898, 73, 267) has a most marked effect on the dyeing properties; this was to be expected, as the compound does not then possess *o*-hydroxyl groups. A third quercetin monomethyl ether has been shown to exist in minute quantity in the *Tamaris Africana* (*Trans.*, 1898, 73, 380), and an attempt is now being made to obtain sufficient substance for the location of its methoxy-group in the above manner.

*Quercetin Tetramethyl and Tetraethyl Ethers.*—These compounds, as Herzig has shown (*Monatsh.*, 1888, 9, 552), when decomposed with alcoholic potash, give respectively protocathechuic acid dimethyl and diethyl ether, and also phenolic compounds which are derivatives of phloroglucinol; to determine the constitution of the latter, their azo-



benzene compounds were examined, with the result that the one derived from quercetin tetramethyl ether was found to be *disazobenzene phloroglucinol monomethyl ether*, m. p. 250—252°

The phenol from the tetraethyl ether gave a disazobenzene compound crystallising in orange-red needles melting at 212—214°:

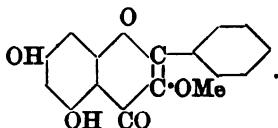
0.0828 gave 0.2015 CO<sub>2</sub> and 0.0365 H<sub>2</sub>O. C = 66.36; H = 4.89.

0.0771 „ 10.5 c.c. nitrogen at 18° and 751 mm. N = 15.53.

(C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H(OH)<sub>2</sub>·OC<sub>2</sub>H<sub>5</sub> requires C = 66.24; H = 4.94; N = 15.47 per cent.

It was evidently *disazobenzene phloroglucinol monomethyl ether*.

*Kampherol Monomethyl Ether*.—A trace of this substance, recently described by Testoni (*Gazzetta*, 1900, 30, ii, 327) as a constituent of Galanga root (*Alpinia officinarum*), was available for examination. When decomposed by the aspiration of air through its alkaline solution, it yielded benzoic acid, (m. p. 121°), and a phenolic compound which gave the phloroglucinol reaction. In the presence of sodium carbonate, this gave an azobenzene compound, identified as trisazobenzene phloroglucinol, and consequently there was no methoxy-group in this portion of the molecule. Adopting the constitution for kampherol suggested by Kostanecki, it is evident that the above methyl ether must be represented as follows:



This method of analysis has already been employed with the decomposition products of the ethers of luteolin (Trans., 1900, 77, 1314), myricetin (Trans., 1902, 81, 203), and genistein (Trans., 1900, 77, 1310), with the result that in all cases the ethers of phloroglucinol were isolated. There is no reason to doubt that the corresponding derivatives of chrysin and apigenin would by similar methods give a like result, and it appeared unnecessary to undertake their preparation for this purpose.

The authors are indebted to the Research Fund Committee of the Chemical Society for a grant which has been in part employed to cover the expense of this research.

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# XLVIII.—*Robinin, Violaquercetin, Myrticolorin, and Osyritrin.*

By ARTHUR GEORGE PERKIN, F.R.S.E.

## *Robinin.*

IN a previous communication (Trans., 1900, 77, 430), it was shown that the leaves of *Robinia Pseudacacia* contain acacetin, a monomethyl ether of apigenin, an interesting point in view of the discovery by Zwenger and Dronke (*Annalen Suppl.*, 1861, 1, 263) that the flowers of the same plant contain a quercetin glucoside, robinin. As these flowers, however, are practically devoid of dyeing properties, it seemed doubtful whether a quercetin compound was present, and reference to the work of these chemists made it probable this suspicion was well founded. At the time of Zwenger and Dronke's investigation, the obstinacy with which these colouring matters retain water of crystallisation was not fully appreciated, and results accurate in themselves frequently received a wrong interpretation. The analyses of their "quercetin" were made with material dried at 100°, a temperature at which it is rarely rendered anhydrous; again, it was unlikely that picric acid would result from the action of nitric acid on quercetin.

Some difficulty was at first experienced in procuring raw material for this investigation, but ultimately this was overcome by the kindness of Dr. J. van Rijn, of Maasstricht, who was good enough to superintend the gathering and drying of some quantity of the flowers.

For isolating robinin, Zwenger and Dronke digested the flowers with boiling water, subsequently evaporating the extract and treating the residue with alcohol. The following method is more rapid, and is suitable for dealing with small quantities of raw material.

The flowers were digested with ten times their weight of boiling alcohol for 4 hours, the mixture strained through calico, and the residue well pressed and again treated in a similar manner. The pale green extract, which deposited a wax on cooling, was concentrated by evaporation, poured into water, and the mixture extracted with ether, the alcohol contained in the aqueous liquid being removed by distillation; on standing overnight, this solution deposited crystals which were collected and washed with a mixture of alcohol and chloroform until the washings were colourless. The residue was then purified by two or three crystallisations from water with the aid of animal charcoal. One hundred and ninety grams of the flowers gave 1.76 grams, or 0.82 per cent., of robinin in the crude condition, this being reduced approximately one-half on purification.

As thus obtained, it consisted of extremely pale yellow needles sinter-

ing at  $190^{\circ}$  and melting at  $196-197^{\circ}$  (Z. and D. 195°), and had the general properties mentioned by these authors. When dried at  $100^{\circ}$ :

0.1103 gave 0.2123  $\text{CO}_2$  and 0.0550  $\text{H}_2\text{O}$ . C = 52.49; H = 5.54.

$\text{C}_{33}\text{H}_{42}\text{O}_{20}$  requires C = 52.24; H = 5.54 per cent.

Zwenger and Dronke assign to robinin at  $100^{\circ}$  the formula  $\text{C}_{25}\text{H}_{30}\text{O}_{16}$  (C = 51.19; H = 5.11), and with this their analytical figures closely agree. This discrepancy suggested that our preparation might contain a trace of free colouring matter which would raise the percentage composition. An alcoholic solution of a second preparation was therefore poured into ether (in which the colouring matter is soluble, but not the glucoside) and the precipitated product collected, again crystallised from water, and dried at  $100^{\circ}$ :

0.1131 gave 0.2165  $\text{CO}_2$  and 0.0575  $\text{H}_2\text{O}$ . C = 52.20; H = 5.64.

The glucoside was thus evidently homogeneous.

Determinations of the water of crystallisation contained in the glucoside dried at the ordinary temperature, employing two distinct preparations, gave the following results:

1.5790, at  $100^{\circ}$ , lost 0.2450  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}$  = 15.51.

1.6079, " " 0.2505  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}$  = 15.58.

$\text{C}_{33}\text{H}_{42}\text{O}_{20} \cdot 8\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$  = 15.97 per cent.

$\text{C}_{33}\text{H}_{42}\text{O}_{20} \cdot 7\frac{1}{2}\text{H}_2\text{O}$  "  $\text{H}_2\text{O}$  = 15.11 "

Air-dried robinin thus crystallises with  $8\text{H}_2\text{O}$ . These results are not in agreement with those of Zwenger and Dronke, who found 14.53 per cent. of water, agreeing with the amount required for the formula  $\text{C}_{25}\text{H}_{30}\text{O}_{16} \cdot 5\frac{1}{2}\text{H}_2\text{O}$ , or according to the above,  $\text{C}_{33}\text{H}_{42}\text{O}_{20} \cdot 7\text{H}_2\text{O}$ . This discrepancy is curious, although the lower figures these authors give for robinin dried at  $100^{\circ}$  suggest the possibility that their product still contained some water of crystallisation.

*Decomposition with Acid.*—The dried glucoside was boiled with dilute sulphuric acid \* for at least 2 hours, and after standing overnight, the liberated colouring matter was collected, washed, and dried at  $100^{\circ}$ :

0.6110, at  $100^{\circ}$ , gave 0.2330 colouring matter. Found, 38.13.

0.9804, " " 0.3745 " " 38.19.

1.2265, " " 0.4650 " " 37.92.

Zwenger and Dronke, on the other hand, found that *air-dried* robinin gave 37.96 per cent. of "quercetin" dried at  $100^{\circ}$ , an amount considerably in excess of that given above. Thus, air-dried robinin,  $\text{C}_{33}\text{H}_{42}\text{O}_{20} \cdot 8\text{H}_2\text{O}$ , should give 33.70 per cent. of the colouring matter  $\text{C}_{18}\text{H}_{10}\text{O}_6 \cdot \text{H}_2\text{O}$ , or but 31.70 per cent. of the anhydrous substance. In their paper, they state that robinin is "extremely easily" decom-

\* 750 c.c. of 1 per cent. solution for each gram of glucoside.

posed by boiling dilute sulphuric or hydrochloric acids, but with acid of 1 per cent. strength this was not found to be the case, for with a short digestion, 39.54 per cent. of "colouring matter" was obtained, a fact suggesting that it was contaminated with unaltered glucoside.

*The Colouring Matter.*—For analysis, the product was recrystallised from dilute alcohol and dried at 160°:

0.1122 gave 0.2589 CO<sub>2</sub> and 0.0355 H<sub>2</sub>O. C = 62.93; H = 3.51.

C<sub>15</sub>H<sub>10</sub>O<sub>6</sub> requires C = 62.93; H = 3.49 per cent.

Zwenger and Dronke found that this colouring matter, dried at 100°, gave C = 59.31, H = 4.49, numbers in close agreement with those required for the formula C<sub>15</sub>H<sub>10</sub>O<sub>6</sub>.H<sub>2</sub>O (C = 59.2, H = 3.94).

Prepared as above, it crystallised in slender, yellow needles melting at 276—278°, readily soluble in boiling alcohol, and soluble in alkaline solutions with a pale yellow colour. For additional proof that it was not quercetin, comparative dyeing trials were carried out employing woollen cloth mordanted with chromium, aluminium, tin, and iron.

	Chromium.	Aluminium.	Tin.	Iron.
Quercetin .....	Red-brown.	Brown-orange-yellow.	Bright orange.	Olive-black.
Robinin colouring matter	Brown-yellow.	Full golden-yellow.	Lemon-yellow.	Deep olive-brown.

With mineral acids in the presence of acetic acid, it yielded crystalline compounds, and to confirm its molecular weight the sulphuric acid derivative was analysed.

0.1556 gave 0.2657 CO<sub>2</sub> and 0.0457 H<sub>2</sub>O. C = 46.57; H = 3.26.

C<sub>15</sub>H<sub>10</sub>O<sub>6</sub>.H<sub>2</sub>SO<sub>4</sub> requires C = 46.87; H = 3.12 per cent.

Alcoholic potassium acetate yielded a *monopotassium* salt, but owing to lack of material this was not fully investigated. The *acetyl* derivative, prepared in the usual manner, crystallised from methyl alcohol in colourless needles:

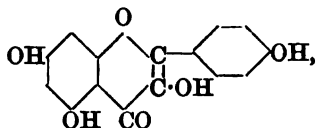
0.1093 gave 0.2438 CO<sub>2</sub> and 0.0400 H<sub>2</sub>O. C = 60.83; H = 4.06.

C<sub>15</sub>H<sub>8</sub>O<sub>6</sub>(C<sub>2</sub>H<sub>3</sub>O)<sub>4</sub> requires C = 60.79; H = 3.96 per cent.

When fused with alkali, the colouring matter gave *p*-hydroxybenzoic acid (m. p. 208—210°) and phloroglucinol.

These facts, together with a comparative dyeing trial, conclusively proved that the colouring matter derived from robinin is identical with that isolated from the flowers of the *Delphinium Consolida* (Proc., 1900, 16, 182). This similarity was corroborated by the peculiar behaviour of their acetyl derivatives when heated; thus, while some preparations melted at 180—182°, others became liquid at about 116°, resolidified as the temperature rose, and finally melted at 180—182°. The colour-

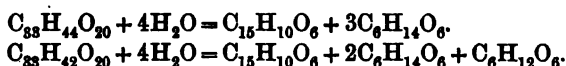
ing matter is in reality *kampherol*, first obtained by Gordin (*Diss. Berne*) by the decomposition of its monomethyl ether *kampheride*, which is contained in galanga root (*Alpinia officinarum*). This, as Kostan-  
ecky suggests (*Ber.*, 1901, 34, 3723), has in all probability the con-  
stitution



and may be considered as the connecting link between apigenin and quercetin. Kampherol, and *not quercetin*, is the colouring matter produced when robinin is hydrolysed with acid.

*The Sugars.*—The acid filtrates formed by the decomposition of robinin were neutralised with barium carbonate, filtered, and evaporated to a small bulk. The product yielded an osazone which after three crystallisations from dilute alcohol was obtained as a spongy mass of yellow needles sintering at 165° and melting at 178—180°. As a further treatment in this manner did not yield a homogeneous substance, it was dissolved in alcohol, the solution poured into ether, and well washed with water. On slow evaporation, a small quantity of crystalline matter separated, and this was collected, washed with ether, and recrystallised from alcohol. It melted at 204—205° and resembled *glucosazone*.

The filtrate which contained the main bulk of the osazone, on spontaneous evaporation, deposited crystals which were extracted with benzene, washed with traces of ether, and recrystallised from dilute alcohol. In the preliminary notice (*Proc.*, 1901, 17, 87), it was considered probable that this substance was *galactosazone*, but fermentation experiments kindly carried out for me by Dr. Turnbull, of the Leather Industries Department, did not corroborate this view. Employing the sugar solution, as obtained in the above manner from robinin, a slight fermentation did indeed occur, but the main bulk was unattacked and gave an osazone melting at 180—182°. This was found to be identical with *rhamnosazone* prepared from pure rhamnose, thus harmonising with the results of Zwenger and Dronke. Whether the trace of the glucose derivative simultaneously isolated is an ingredient of robinin itself or is derived from a second glucoside of kampherol also present in minute quantity must, although it appears unlikely, remain a matter for conjecture. Very large quantities of raw material would be required to decide this point. According to these views, the formula of robinin is consequently either  $C_{33}H_{44}O_{20}$  or  $C_{33}H_{42}O_{20}$ , and its decomposition by acid may be represented as follows:



It is thus a most interesting glucoside, as it appears to be the first known substance of this class to contain three sugar nuclei. The above equations require respectively a yield of 37·63 and 37·73 per cent. of kampherol, whereas that actually obtained was 38·13, 38·19, and 37·92 per cent.

Dyeing experiments carried out in the usual manner with woollen cloth showed that robinin is almost devoid of tinctorial properties; this was to be expected from the preliminary examination of the flowers.

*The Identity of Osyritrin, Violaquercitrin and Myrticolarin.*

In a previous communication (Trans., 1897, 71, 1132), it was shown that the leaves of the *Colpoön compressum* contain a quercetin glucoside, osyritrin, to which, dried at 130°, the formula  $\text{C}_{27}\text{H}_{30}\text{O}_{17}$  was assigned. At that time, the raw material available yielded little more than 1 gram of the pure substance, but subsequently, through the kindness of Mr. R. H. Coaton, of Wellington, Cape of Good Hope, a larger supply was obtained, and it became possible to investigate it more fully.

*Water of Crystallisation.*—For determining the loss of weight which the air-dried glucoside undergoes, it was exposed for about three weeks over sulphuric acid in a desiccator. As the product on exposure to the atmosphere rapidly assumed its original weight, the analysis was performed indirectly in this manner.

1·3345, dried as above, gained 0·0770  $\text{H}_2\text{O}$ . Found 5·76.

$\text{C}_{27}\text{H}_{30}\text{O}_{17} \cdot 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 5·44$  per cent.

At 130°, employing an oil-bath jacketed with amyl alcohol (b. p. 130—131°), it suffered a further loss of 0·0200  $\text{H}_2\text{O}$ , or 1·49 per cent. ( $\frac{1}{2}\text{H}_2\text{O}$  requires 1·43) and finally, at 160° (oil-bath jacketed with turpentine), 0·0220 gram  $\text{H}_2\text{O}$  was evolved, or 1·67 per cent. ( $\frac{1}{2}\text{H}_2\text{O} = 1·47$ ). Osyritrin, therefore, crystallises from water with 3 mols. of water of crystallisation.

Anhydrous osyritrin is remarkably hygroscopic, thus, on exposure for 1 hour in the air of the room, it completely regains its water of crystallisation. On analysis:

0·1170 gave 0·2275  $\text{CO}_2$  and 0·0537  $\text{H}_2\text{O}$ . C = 53·03; H = 5·09.

$\text{C}_{27}\text{H}_{28}\text{O}_{16}$  requires C = 53·28; H = 4·60 per cent.

Decomposed with dilute sulphuric acid:

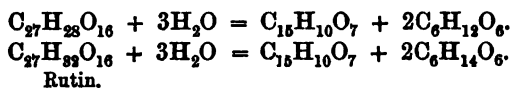
0·8400 gave 0·4137  $\text{C}_{15}\text{H}_{10}\text{O}_7$ . Found 49·25.

$\text{C}_{27}\text{H}_{28}\text{O}_{16}$  requires  $\text{C}_{15}\text{H}_{10}\text{O}_7 = 49·67$  per cent.



The osazone of the sugar melted at 204—205°, as previously found, and was evidently glucosazone.

Osyritrin dried at 160° has thus the formula  $C_{27}H_{28}O_{16}$ , and at 130°  $(C_{27}H_{28}O_{16})_2 \cdot H_2O$ , and not  $C_{27}H_{30}O_{17}$  as formerly suggested. Its hydrolysis with acid is analogous to that of rutin, which in a similar manner gives quercetin and rhamnose (Schunck, Trans., 1888, 53, 264):



### *Violaquercitrin.*

Mandelin (*Jahresber.*, 1883, 1369) isolated this glucoside from the flowers of the *Viola tricolor variensis*, and assigned to it the formula  $C_{42}H_{42}O_{24}$ . It has been previously pointed out that this is more correctly  $C_{27}H_{28}O_{16}$ , as the true molecular weight of quercetin was not known at that time.

For its preparation from the flowers, a method identical with that employed for the preparation of osyritrin (*loc. cit.*) gave an excellent result:

0.1071, dried at 130°, gave 0.2036  $CO_2$  and 0.0510  $H_2O$ .  $C = 51.84$  ;  
 $H = 5.29$  per cent.

0.1144, dried at 160°, gave 0.2230  $CO_2$  and 0.0535  $H_2O$ .  $C = 53.16$  ;  
 $H = 5.19$  per cent.

As Mandelin employed water for the isolation of his substance, it seems possible that the result he obtained was due to the contamination of his product with a trace of quercetin.

*Water of Crystallisation.*—When dried over sulphuric acid, 0.9702 gained, on exposure to the atmosphere, 0.0580  $H_2O$ . Found  $H_2O = 5.64$  ;  $2H_2O$  requires 5.44 per cent.

1.0280, at 130°, lost 0.070  $H_2O$ .  $H_2O = 6.80$ .

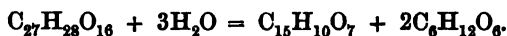
$2.5H_2O$  requires  $H_2O = 6.79$  per cent.

1.0280, at 160°, lost 0.085  $H_2O$ .  $H_2O = 8.26$ .

$3H_2O$  requires  $H_2O = 8.16$  per cent.

Violaquercitrin thus crystallises with  $3H_2O$ .

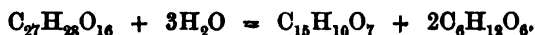
When dried at 160° and decomposed with acid, it gave 49.35 per cent. of quercetin, which is in accordance with the following equation (49.67 per cent.):



The osazone of the sugar melted at 204—205° and was evidently glucosazone. Violaquercitrin melts at 186° when slowly and at 190° when rapidly heated, and is undoubtedly identical with osyritrin.

***Myrticolorin.***

This quercetin glucoside was isolated by H. G. Smith (Trans., 1898, 73, 697) from the leaves of the *Eucalyptus macrorhyncha*, who assigned to it the formula  $C_{27}H_{28}O_{16}$ , and represented its decomposition with acid by the equation



Smith at first considered the sugar thus produced (*loc. cit.*) to be galactose, but more recently, in a private communication, he informs me that this is not the case, as he has obtained from it glucosazone, (m. p. 204—205°). It is worthy of note that he (*loc. cit.*) calls attention in his paper to the remarkable similarity of myrticolorin to osyritrin.

The raw material employed was some commercial myrticolorin, for which I am indebted to the kindness of Mr. Smith. After purification, a sample dried at 160° gave C=53.03 and H=5.09 per cent., and on decomposition with acid 49.25 per cent. of quercetin :

Dried over sulphuric acid, on exposure to air it gained  $H_2O = 5.76$  percent.

and heated at 130° it lost  $H_2O = 1.49$  per cent.  
Dried at 130° and heated at 160° it lost  $H_2O = 1.67$  per cent.

Myrticolorin, therefore, crystallises from water with  $3\text{H}_2\text{O}$ , and this may be fractionally removed by methods identical with those employed in the case of osyritrin. As the melting points, general reactions, and dyeing properties also agree, there can be no doubt that *the substances are identical*, moreover, it was previously shown (Trans., 1899, 75, 433) that osyritrin, violaquercitrin, and myrticolorin give, by means of potassium acetate, monopotassium derivatives (found  $K=6.21$ ). There is no doubt, therefore, that these also must be regarded as one of the same compound, represented by the formula  $\text{C}_{27}\text{H}_{27}\text{O}_{16}$  ( $K=6.03$  per cent.).

Certain glucosides, as ruberythric acid and the purpurin glucoside contained in madder are decomposed during the dyeing operation by means of the mordant, which combines with the alizarin or purpurin thus liberated. Such, however, I find is not the case with the known glucosides of the quercetin group, which are dyestuffs of themselves, and give shades differing considerably in most cases from those yielded by the colouring matters from which they are derived.\* A simple experiment with persian berries clearly illustrates this point. This dye contains glucosides of rhamnetin, rhamnazin, and quercetin, and

\* Nietzki ("Chemistry of Organic Dye-stuffs," 1892, 255) considers it probable that in dyeing the quercitrin splits up, and that the shades obtained are due to the formation of quercetin lakes.

there is also present a ferment which at about 40° in the presence of water hydrolyses these compounds; if, therefore, the dye-bath be raised slowly to the boiling point, this change occurs, and the resulting shade is due to the free colouring matters and not to the glucosides. On the other hand, if the berries be plunged into boiling water, the activity of the ferment is at once destroyed, and the tinctorial property of this extract is now due to the glucosides as the shade indicates. This difference is very similar to that shown between quercetin and its glucosides, which gave the following results with woollen cloth mordanted in the usual manner:

	Chromium.	Aluminium.	Tin.	Iron.
Quercitrin ...	Full brown-yellow.	Full golden-yellow.	Lemon-yellow.	Deep olive.
Quercetin ...	Red-brown.	Brown-orange, inclining to red.	Bright orange.	Olive-black.
Osyritrin ...	Brown-yellow.	Full golden-yellow.	Lemon-yellow.	Dull brown.
Rutin.....	Brown-yellow.	Full golden-yellow.	Lemon-yellow.	Dull brown.

It is interesting to observe that rutin and osyritrin have identical tinctorial properties, which points to the fact that the two sugar nuclei of each (in the one case rhamnose and the other dextrose) are similarly attached to the quercetin residue. As regards their actual disposition, satisfactory proof is at present wanting, but it is highly probable that one at least is attached to the catechol group, as the dyeing properties suggest the absence of *o*-hydroxyl groups. Their behaviour with potassium acetate is an indication that they contain intact the hydroxyl of the pyrone ring, for it is found that galangin, by this method, forms a monopotassium salt. The properties as a whole would harmonise closely with those of a compound containing both sugar nuclei attached to the catechol group, but further evidence is needed before this conclusion can be adopted.

CLOTHWORKERS' RESEARCH LABORATORY,  
DYEING DEPARTMENT,  
YORKSHIRE COLLEGE.

## XLIX.—*The Influence of Salts and other Substances on the Vapour Pressure of Aqueous Ammonia Solution.*

By EDGAR PHILIP PERMAN.

THE author recently published a series of measurements of the vapour pressure of aqueous ammonia solution showing the effect of alteration of concentration for certain selected temperatures (Trans., 1901, 79, 718). These results may, of course, be looked at in another way,

namely, as expressing the solubility of ammonia under varying pressure, and it may be well to compare them with the results of other investigators in this line of research.

Roscoe and Dittmar (*Annalen*, 1859, 112, 349) determined the solubility at  $0^{\circ}$  at pressures varying from 18 mm. to 1963 mm. The pressures given are "partial pressures" obtained by subtracting the vapour pressure of water at the temperature of the experiment from the total pressure. It may be pointed out that this method of calculating partial pressure is quite inadmissible, for the ammonia solution may be regarded as a mixture of two liquids, and the total vapour pressure would be equal to the sum of the vapour pressures of the liquids taken separately only if they were completely immiscible. (The author is already engaged in determining the partial pressures of the ammonia and the water in an aqueous ammonia solution.) On adding the vapour pressure of water to the pressures recorded, the few results available for comparison agree well with those given by the author in his previous paper.

Sims (*Annalen*, 1861, 118, 345) found the solubility of ammonia in water at  $0^{\circ}$ ,  $20^{\circ}$ ,  $40^{\circ}$ , and  $100^{\circ}$ . The results are somewhat scanty, but free use was made of graphic interpolation. The pressures given are "partial," as in the previously named paper; when corrected to total pressure, the numbers are much lower than those obtained by me.

Watts (*Annalen Suppl.*, 1865, 3, 227) made experiments at  $0^{\circ}$  and  $20^{\circ}$  with a mixture of ammonia and air; when corrected to total pressures, as before, the results fall almost exactly on the curves representing the results of my experiments.

Raoult (*Ann. Chim. Phys.*, 1874, [v], 1, 262) made some single determinations at temperatures from  $0^{\circ}$  to  $28^{\circ}$  at a "partial pressure" of 760 mm. They cannot well be compared with those under consideration.

Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1894, 26, 48), as the result of experiments of which the numbers are not given, states that aqueous solutions of ammonia do not follow Dalton's law at the ordinary temperature, but with rise of temperature the disagreement becomes less, until at  $100^{\circ}$  the numbers are in accord with this law. This result was obtained approximately also by Sims. Konowaloff (*ibid.*, 1899, 31, 910) has also found the partial pressures of some solutions at  $60^{\circ}$  by the dynamical method, but the solutions used were so weak that the results are not comparable with mine.

The outcome of this comparison, so far as it can be carried out, is a confirmation of the accuracy of the numbers given in the previous paper, except in the case of the results obtained by Sims, which are probably erroneous.

Much work has also been done on the vapour pressure of ammonia

and salt solutions. Raoult (*loc. cit.*) investigated the solubility of ammonia in solutions of potassium hydroxide, sodium hydroxide, ammonium chloride, ammonium nitrate, sodium nitrate, and calcium nitrate respectively, and his results, briefly summarised, are:

(1) Potassium and sodium hydroxides greatly lessen the solubility; equivalent quantities have the same effect, and the effect of each is proportional to the amount present in a given volume.

(2) Ammonium chloride also decreases the solubility proportionally to the amount present.

(3) Ammonium and sodium nitrates have practically no effect on the solubility.

(4) Calcium nitrate increases the solubility in proportion to the amount present, but the effect of alteration of pressure on the solution is nearly the same as on an ammonia solution.

(5) Experiments on the heat of solution of ammonia in solutions of these substances appeared to show that they were approximately the same as the heat of solution in water.

Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 910) found by the dynamical method the effect of the presence of a number of salts on the partial pressure of the ammonia. The decrease in the pressure of the ammonia can be expressed by the formula

$$H = H_1 (n - km) \text{ where}$$

$H_1$  = pressure of the ammonia in pure aqueous solution of less than  $1\frac{1}{2}$  normal strength.

$H$  = pressure of the ammonia in solution containing the salt.

$n$  = number of gram-molecules of ammonia per litre.

$m$  = " " " salt per litre.

For silver nitrate  $k = 2$ , and for cadmium nitrate, zinc nitrate, nickel chloride, copper nitrate, copper chloride, copper sulphate, and copper acetate, the value of  $k$  approaches  $H$ . This is taken to indicate the presence of complexes like  $\text{AgNO}_3 \cdot 2\text{NH}_3$ ;  $\text{CuSO}_4 \cdot 4\text{NH}_3$  in solution.

Gaus (*Zeit. anorg. Chem.*, 1900, 25, 236), by a very interesting modification of the dynamical method, has determined the influence of a number of salts on the partial pressure of the ammonia, the results agreeing with those already mentioned. Ammonium nitrate and barium chloride produce hardly any effect. Copper sulphate causes a large depression which is proportional to the amount of salt present. Quite recently this work has been largely extended by Abegg and Riesenfeld (*Zeit. physikal. Chem.*, 1902, 40, 84).

A consideration of the work of these investigators as well as that of Dawson and McCrae (*Trans.*, 1900, 77, 1239), seems to indicate clearly the existence of metal ammonia complexes in solution, notwithstanding the opinion of Raoult concerning calcium nitrate, but the effect of salts

which would not be expected to have any chemical action has not yet been explained.

The experiments about to be described were directed towards the elucidation of (1) the effect of substances having no direct chemical action on the ammonia, (2) the effect of change of temperature on the copper sulphate ammonia solution, (3) the existence, or otherwise, of hydrates in solution.

The method was very nearly the same as that described in a previous paper (*loc. cit.*, p. 725) except that the vapour jacket was replaced by a water-bath with a toluene gas regulator; the temperature did not usually vary more than  $0.01^{\circ}$  during an experiment. The height of the mercury column, as well as that of the ammonia solution above it, was read by means of a mirror scale placed in front of the bath at an angle so that the reflection of the mercury could be easily read. With this arrangement, parallax can be easily avoided by making the scale line nearest the reading coincide with its reflection.

#### *Influence of Substances having no direct Chemical Action on Ammonia.*

Substances having no direct action on ammonia are hard to find; those employed as likely to have no action were urea, mannitol, potassium sulphate, and ammonium chloride. A preliminary experiment was made to discover whether urea undergoes any decomposition when heated with ammonia solution; 20 grams of urea were heated in a sealed tube with an aqueous ammonia solution of about four times normal strength at  $40^{\circ}$  for 6 hours. Before heating, 10 c.c. of the solution required (1) 41.98 c.c., (2) 42.07 c.c., and after heating (1) 41.90 c.c., (2) 41.90 c.c. of normal sulphuric acid solution for neutralisation.

To determine the vapour pressures, a solution was made containing a weighed quantity of urea (or other substance) and the ammonia then estimated by titration; after the vapour pressures had been measured, the ammonia was again estimated, and in every case the amount agreed well with the previous result. After the solution had been transferred to the vessel for measuring the pressures, the air was driven out of it by repeatedly lowering the pressure (by lowering the open tube containing mercury) and then driving out the liberated air by raising the mercury quickly and opening the stopcock at the top for a moment.

The pressures for a corresponding ammonia solution have been found by reading off the values for the particular strength on the curves given in the previous paper. These give values of pressure for  $0^{\circ}$ ,  $20^{\circ}$ ,  $34.4^{\circ}$ ,  $46.4^{\circ}$ , and  $61.3^{\circ}$ . From these, a curve was constructed which may be called an *isothen* or line of equal strength, and from it

the pressures for the temperatures employed were read off. The strength of the corresponding ammonia solution has been calculated in two ways (I) as a solution containing the same proportion of ammonia to water, (II) as a solution containing the same mass of ammonia in unit volume of the solution. Both are given where possible in the following tables.

*Urea Solution I.*— $\text{NH}_3$ , 16.36;  $\text{CO}(\text{NH}_2)_2$ , 10.43;  $\text{H}_2\text{O}$ , 73.21 per cent. Density, 0.9591 at 22°. Strength of corresponding  $\text{NH}_3$  solution, (I) 18.26, (II) 16.73 per cent. :

Temperature.	Pressure in mm.	Aqueous $\text{NH}_3$ solution.	
		Pressure I in mm.	Pressure II in mm.
24.58°	255.4	258	221
29.39	312.0	318	276
35.20	403.0	405	354
40.38	496.8	500	438
45.59	611.4	611	532
54.43	856.1	854	738
59.07	1014.4	1008	880

*Urea Solution II.*— $\text{NH}_3$ , 17.22;  $\text{CO}(\text{NH}_2)_2$ , 5.29;  $\text{H}_2\text{O}$ , 77.49 per cent. Density, 0.9425 at 21°. Strength of corresponding  $\text{NH}_3$  solution (I) 18.18, (II) 17.38 per cent. :

Temperature.	Pressure in mm.	Aqueous $\text{NH}_3$ solution.	
		Pressure I in mm.	Pressure II in mm.
25.05°	260.4	263	240
29.58	316.6	322	294
34.96	400.3	402	373
39.68	485.1	485	452
45.90	621.8	618	569
50.07	726.2	722	659
54.45	856.9	854	775
58.00	973.7	970	886

When the vapour pressure of the urea-ammonia solution is compared with that of an aqueous ammonia solution having the same ratio of ammonia to water, the agreement is remarkable, but when it is compared with that of a solution containing the same amount of ammonia in a given volume, the apparent effect of the urea is to decrease the solubility of the ammonia. This may be due simply to the increase in volume of the solution on addition of the urea.

*Mannitol Solution.*— $\text{NH}_3$ , 12.27; mannitol, 4.56;  $\text{H}_2\text{O}$ , 83.17 per cent. Density, 0.9636 at  $15^\circ$ . Corresponding  $\text{NH}_3$  solution, (I) 12.86, (II) 12.43 per cent. :

Temperature.	Pressure in mm.	$\text{NH}_3$ solution.	
		Pressure I in mm.	Pressure II in mm.
22.92°	143.8	150	141
29.77	197.7	205	196
36.78	271.2	275	262
42.74	348.8	355	332
50.61	479.1	484	453
57.79	629.6	636	595

When the vapour pressure of the mannitol-ammonia solution is compared with that of an aqueous ammonia solution, a small but regular decrease is shown, due, possibly, to the formation of a compound of mannitol and ammonia. Mannitol is known to form stable compounds with the alkaline earths.

*Potassium Sulphate Solution.*— $\text{NH}_3$ , 7.49;  $\text{K}_2\text{SO}_4$ , 3.05;  $\text{H}_2\text{O}$ , 89.46 per cent. Density, 0.9826 at  $35^\circ$ .  $\text{NH}_3$ , 7.73 per cent. of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  :

Temperature.	Pressure in mm.	Pressure of 7.73 per cent. $\text{NH}_3$ solution in mm.
40.42°	203.5	192
46.70	265.2	250
51.14	320.0	302
58.51	427.5	407

It was difficult to make a suitable solution owing to the slight solubility of the potassium sulphate, and with the solution employed the measurements could not be begun below  $40^\circ$ . The large increase in pressure may be due to a displacement of ammonia molecules by salt molecules, or possibly to the formation of hydrates producing a concentration of the solution. Potassium and sodium chlorides were found by Gaus to increase the pressure largely, and the hydroxides still more. The increase in pressure must be ascribed to the change in the nature of the solvent, and the relation between the two changes reserved for further investigation.

*Ammonium Chloride Solution I.*— $\text{NH}_3$ , 16.85;  $\text{NH}_4\text{Cl}$ , 5.27;  $\text{H}_2\text{O}$ , 77.88 per cent. Density, 0.9472 at  $14^\circ$ . Corresponding  $\text{NH}_3$  solution, (I) 17.79, (II) 17.07 per cent. :



Temperature.	Pressure in mm.	NH <sub>3</sub> solution.	
		Pressure I in mm.	Pressure II in mm.
19·01°	(182·1)	183	169
26·04	251·1	263	245
32·93	343·0	355	333
39·24	449·3	457	430
49·26	667·2	675	622
57·83	913·2	933	860

*Ammonium Chloride Solution II.*—NH<sub>3</sub>, 12·90; NH<sub>4</sub>Cl, 10·26; H<sub>2</sub>O, 76·84 per cent. Density, 0·9724 at 16°. Corresponding NH<sub>3</sub> solution, (I) 14·37, (II) 13·24 per cent. :

Temperature.	Pressure in mm.	NH <sub>3</sub> solution.	
		Pressure I in mm.	Pressure II in mm.
23·12°	158·5	171	154
30·89	230·5	243	223
38·26	318·5	334	301
45·37	428·8	447	402
51·18	543·2	560	502
58·14	707·6	723	651

If the results are compared with those obtained with ammonia solution I, the ammonium chloride is seen to produce a decrease in pressure, and the decrease is approximately twice as much in solution II as in I (except at the low temperatures, where there seems to be some experimental error in solution I). This suggests the formation of some compound of the ammonia with the ammonium chloride. Since the completion of these experiments, the author has found that compounds such as NH<sub>4</sub>Cl,3NH<sub>3</sub> and NH<sub>4</sub>Cl,6NH<sub>3</sub> have been isolated (*Compt. rend.*, 1879, 88, 578), and it is probably due to the formation of compounds like these that the vapour pressure of the solution is diminished.

Gaus found barium chloride and ammonium nitrate to have only a very slight effect on the ammonia pressure, and Raoult found ammonium nitrate and potassium nitrate to have none; Raoult's experiments, however, were carried out with such strong solutions that they are hardly comparable with those now described.

From the results hitherto obtained, it seems impossible to predict what effect will be produced by introducing into the solution a sub-

stance which would be expected to have no direct chemical action on the ammonia; the influence, however, would appear to be small except in the case of salts of the alkalis. If, however, a substance, as, for example, silver chloride or zinc sulphate, is known to form a definite compound with ammonia, the pressure of the ammonia is invariably diminished, but the effect of the ammonia going into combination may be complicated by other effects not yet understood.

*Effect of Change of Temperature on a Solution of Cupri-ammonium Sulphate.*

It was found necessary to use weak ammonia solutions, otherwise a sufficient amount of copper sulphate could not be kept in solution at the lower temperatures. An attempt was made to measure the vapour pressure at 0°, but without success; the height of the mercury column could not be read, for the solution stuck to the glass and the mercury rose inside it. This phenomenon, which is presumably a surface-tension effect, did not occur at about 20°.

*Copper Sulphate Ammonia Solution I.*— $\text{NH}_3$ , 14.65;  $\text{CuSO}_4$ , 2.68;  $\text{H}_2\text{O}$ , 82.67 per cent. Density, 0.9652 at 15°. Corresponding  $\text{NH}_3$  solution (I) 15.05, (II) 15.01 per cent. :

Temperature.	Pressure in mm.	Pressure $\text{NH}_3$ solution in mm.	Pressure of $\text{NH}_3$ solution in mm.
18.88°	138.6	145	138 } subtracting 3 $\text{NH}_3$
26.37°	197.6	212	197 } mols. for each mol.
36.08	306.9	324	303 } $\text{CuSO}_4$ .
43.64	421.6	446	419 }
47.49	492.6	518	491 } „ 2 $\text{NH}_3$ „
50.81	559.9	588	555 }
56.54	692.6	725	{ 686 } „ 1 $\text{NH}_3$ „
			{ 700 }

The copper sulphate produces a large decrease in the pressure, in all probability due to the formation of a cupri-ammonium compound. If the copper sulphate in the solution combines with ammonia, forming the compound  $\text{CuSO}_4 \cdot 4\text{NH}_3$ , the amount of free ammonia remaining in the solution can be calculated by subtracting 4 mols.  $\text{NH}_3$  for every  $\text{CuSO}_4$  mol.; an aqueous ammonia solution calculated of this strength has lower pressures than any found for the copper-ammonium sulphate solution at the same temperatures. Subtracting 3 mols.  $\text{NH}_3$ , the pressures coincide at 19° and 26°; subtracting 2 mols.  $\text{NH}_3$ , the pressures are nearly coincident at 44° and 47°. There is evidently progressive dissociation, until at 56.5° only about  $1\frac{1}{2}$  mols.  $\text{NH}_3$  for

every  $\text{CuSO}_4$  mol. remain in combination. Unfortunately, a great assumption has to be made in calculating out these numbers, namely, that the copper sulphate has no influence on the pressure other than that caused by the ammonia going into combination with it. The uncertainty in this matter makes it useless to develop the theory of the decomposition from the numbers obtained. The compound at first in solution is probably  $\text{SO}_2 \left\langle \begin{smallmatrix} \text{O} \cdot \text{NH}_3 \cdot \text{NH}_3 \\ \text{O} \cdot \text{NH}_3 \cdot \text{NH}_3 \end{smallmatrix} \right\rangle \text{Cu}$ , which dissociates into  $\text{SO}_2 \left\langle \begin{smallmatrix} \text{O} \cdot \text{NH}_3 \\ \text{O} \cdot \text{NH}_3 \end{smallmatrix} \right\rangle \text{Cu}$ , and very possibly  $\text{SO}_2 \left\langle \begin{smallmatrix} \text{O} \cdot \text{NH}_3 \cdot \text{NH}_3 \\ \text{O} \text{---} \text{NH}_3 \end{smallmatrix} \right\rangle \text{Cu}$ , is also formed.

On evaporation of the ammonia, or on dilution of the solution, decomposition takes place, probably thus :



These compounds will also be more or less ionised.

*Copper Sulphate Ammonia Solution II.*— $\text{NH}_3$ , 6.54;  $\text{CuSO}_4$ , 3.94;  $\text{H}_2\text{O}$ , 89.52 per cent. Density, 1.010 at 15°. Corresponding  $\text{NH}_3$  solution, (I) 6.81, (II) 6.80 per cent. :

Temperature.	Pressure in mm.	Pressure $\text{NH}_3$ solution in mm.	Pressure $\text{NH}_3$ solution in mm.
30.57	91.8	112	93
36.97	126.2	148	124
41.51	155.1	180	154
46.85	194.7	227	197
52.61	250.1	294	251
57.68	308.8	367	313

} Subtracting  $3\text{NH}_3$

In this case, the amount of ammonia held in combination by the copper is apparently the same as before, but no dissociation takes place, no doubt owing to the much smaller proportion of water with regard to the copper sulphate. After each experiment was completed, the copper solution was tested for mercury, but only a trace was found in each case.

#### *The Existence of Hydrates in Solution.*

The experiments on potassium sulphate before described have an interesting bearing on this question. The author has shown in a recent paper (Trans., 1901, 79, 725) that anhydrous sodium sulphate has a great effect in raising the ammonia pressure, but it is now found that potassium sulphate has a similar effect. The experimental data available for the comparison are given in the table on page 489.

From these numbers we find that the ratio  $\frac{\text{number mols. Na}_2\text{SO}_4}{\text{number mols. K}_2\text{SO}_4} = 1.71$ ,

Composition of solution.	Temperature.	Pressure in mm.	Pressure of corresponding $\text{NH}_3$ solution in mm.	Per cent. increase of pressure.
$\left\{ \begin{array}{l} \text{K}_2\text{SO}_4 \quad 3\cdot05 \\ \text{NH}_3 \quad 7\cdot49 \\ \text{H}_2\text{O} \quad 89\cdot46 \end{array} \right\}$	$40\cdot42^\circ$ $46\cdot70$	203\cdot5 265\cdot2	192 250	5\cdot99 6\cdot08
$\left\{ \begin{array}{l} \text{Na}_2\text{SO}_4 \quad 4\cdot25 \\ \text{NH}_3 \quad 9\cdot90 \\ \text{H}_2\text{O} \quad 85\cdot85 \end{array} \right\}$	$40\cdot42$ $46\cdot70$	276 360	246 320	12\cdot2 12\cdot5

whilst the ratio  $\frac{\text{per cent. increase of press. caused by the } \text{Na}_2\text{SO}_4}{\text{per cent. increase of press. caused by the } \text{K}_2\text{SO}_4} = 2\cdot05$  ( $2\cdot04$  at  $40\cdot42^\circ$  and  $2\cdot06$  at  $46\cdot70^\circ$ ).

These ratios are sufficiently near to each other to show that molecular proportions of potassium sulphate, which crystallises without water, and of anhydrous sodium sulphate have approximately the same effect. There is no difference, such as would be caused by one forming a hydrate in solution and the other not. Supposing the sodium sulphate to take up 10 mols. of water, the concentration of the solution thereby produced would cause an increase in pressure of about 10 per cent.

The increase of pressure caused by the potassium sulphate is 6 per cent., and the number of molecules of sodium sulphate is  $1\cdot7$  times as great as the number of potassium sulphate molecules; the effect of the sodium sulphate should therefore be (supposing molecular proportions to have the same effect) an increase of pressure of  $6 \times 1\cdot7 = 10\cdot2$  per cent.: adding this to the 10 per cent. for the increase in concentration of the solution, we obtain a total increase of 20\cdot2 per cent. This, divided by the increase for the potassium sulphate (6 per cent.), gives 3\cdot37 for the ratio  $\frac{\text{increase by } \text{Na}_2\text{SO}_4}{\text{increase by } \text{K}_2\text{SO}_4}$  instead of 2\cdot05, the number found, a difference far beyond the limits of experimental error.

There is little reason for supposing potassium sulphate to form a hydrate in solution, so that these experiments seem to indicate the non-existence of a hydrate of either sodium sulphate or potassium sulphate in solution.

The experimental part of the work here described was carried out at the Physikalisch-chemisches Institut, Leipzig, and the author wishes to acknowledge the great facilities there afforded him.

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VOL. LXXXI.

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L.—*The Nitration of s-Trihalogen Anilines.*

By K. J. P. ORTON.

IN the hope of possibly throwing further light on the process of substitution in anilines, I have studied the carefully regulated action of nitric acid on those anilines in which chlorine or bromine occupies the positions 2, 4, and 6 in the benzene nucleus relatively to the amino-group; namely, those positions into which a substituting group most readily finds its way. That the nitro-group is capable of displacing bromine, at least, from these positions in phenols has been shown by Armstrong and Harrow (*Trans.*, 1876, 30, 448), who obtained 2:6-dibromo-4-nitrophenol and 2-bromo-4:6-dinitrophenol from *s*-tribromophenol. Thiele and Eichwede (*Annalen*, 1900, 311, 363), by the action of amyl nitrite on this phenol, replaced, not the para-, but an ortho-bromine atom, 2:4-dibromo-6-nitrophenol being thus formed. Further, from *s*-tribromoaniline by the action of nitric acid, Losanitsch (*Ber.*, 1882, 15, 474) obtained 2:6-dibromo-4-nitroaniline.

In their behaviour\* with nitric acid (diluted with acetic acid), the anilines investigated divide themselves sharply into two classes; (1) anilines with a bromine atom in the para-position relatively to the amino-group, *s*-tribromoaniline, 2-chloro-4:6-dibromoaniline, and 2:6-dichloro-4-bromoaniline, (2) anilines with a chlorine atom in the para-position relatively to the amino-group, 4-chloro-2:6-dibromoaniline, 2:4-dichloro-6-bromoaniline, and *s*-trichloroaniline. The crystalline aniline nitrate initially formed dissolves on heating, producing solutions of characteristically different colours in the two classes; when a bromine atom is in the para-position, the solution is finally *orange-yellow*; when a chlorine atom is in the para-position, the solution is finally *crimson* (see experimental part). From anilines of the first class, bromine is evolved, and there is obtained a product which possesses a nitro-group in the para-position instead of an atom of bromine. The amount of the dihalogen-nitroaniline represents about 75 per cent. of the original *s*-trihalogen aniline. From anilines of the second class, neither chlorine nor bromine is evolved, nor is an aniline obtained in which a nitro-group has replaced the *p*-chlorine atom. Further, in no case was the replacement of an *o*-bromine atom observed. In this respect, the behaviour of these anilines with nitric acid is analogous to their behaviour with acetylchloroamino-

\* In these experiments, an investigation of the *final* products of the action of nitric acid on these anilines was not intended. This has been done in the case of *s*-tribromoaniline by Losanitsch (*loc. cit.*), dibromodinitromethane, tetrabromobenzene, bromanil, oxalic and picric acids being isolated. Doubtless, these similarly constituted substances undergo degradation in much the same manner.

benzenes, when only the *p*-bromine atom is replaced by chlorine (Trans, 1901, 79, 822). From 2:3:4:6-tetrabromoaniline in which one meta-position is also occupied by bromine, only 2:3:6-tribromo-4-nitroaniline is formed, although replacement of an *o*-bromine atom might be expected from analogy with the action of chlorine, bromine, and nitric acid on meta-substituted anilines, and anilides, which always yield a considerable proportion of the ortho-derivative.

Lastly, in no case was hydrogen in the meta-position replaced by the nitro-group under the conditions employed.

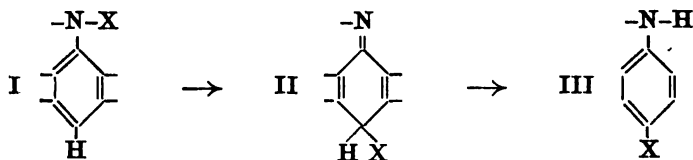
During the period of heating of the acetic acid solution of the aniline and nitric acid (aniline nitrate), there is present a small amount of the nitroamine of the aniline, thus from *s*-trichloroaniline is obtained 1-nitroamino-2:4:6-trichlorobenzene,  $C_6H_2Cl_3 \cdot NH \cdot NO_2$ . These nitroamines would appear to be formed in this reaction by the elimination of water from the aniline nitrate, just as aniline acetates on heating lose water and become acetylamine-derivatives.\* At no period of the experiment did the nitroamine amount to more than 5—10 per cent. of the aniline used. As under the conditions, namely, heating in acetic acid solution in the presence of a mineral acid, the nitroamines themselves undergo change, no great quantity can at *any one time* be present. When a nitroamine in which a bromine atom is in the para-position relatively to the amino-group is dissolved in acetic acid to which one or two drops of sulphuric acid have been added, the nitro-group is transferred to the nucleus and displaces the *p*-bromine atom; † whereas a nitroamine with a chlorine atom in the para-position, under identical treatment, yields no nitroaniline but gives a deep crimson solution, similar in appearance to that obtained directly from the aniline and nitric acid. From the crimson solutions from both sources, red *substances* can be isolated in very small amount; these have not yet been obtained in sufficient quantity for a thorough analysis or investigation. Experiments are now in progress having as their object the preparation of these compounds.

Up to the point of the formation of the nitroamine from the aniline nitrate, there is a complete parallelism in the action of nitric acid on these two classes of *s*-trihalogen anilines (namely, the one class with a *p*-bromine atom and the other with a *p*-chlorine atom); as the nitroamines in each class are under an identical influence, the tendency

\* So far as I am aware *s*-trisubstituted nitroaminobenzenes have not hitherto been prepared; nor have nitroaminobenzenes been obtained by the direct action of nitric acid on anilines. These substances were prepared by Bamberger, Pinnow, and others, by oxidation of alkaline solutions of benzenediazotates, by the action of nitrogen pentoxide on anilines in chloroform solution, and by adding the dry aniline nitrate to acetic anhydride.

† By a similar means, Bamberger brought about the transformation of nitroaminobenzenes into *o*- and *p*-nitroanilines.

in each case must be for the nitro-group to replace the *p*-halogen atom. It was suggested (*loc. cit.*) that in the transformation of the acetylchloro- and acetyl bromo-aminobenzenes (I), into *o*- and *p*-chloro- and bromo-acetanilides (III), an iminoquinone (II) formed a transient intermediate stage.



From this point of view (which was originally foreshadowed by Lapworth, *Trans.*, 1898, 73, 450), it would be expected that both with a *p*-bromo-, and a *p*-chloro-aniline the nitroamine would pass into an iminoquinone in which both the nitro-group and the bromine atom are attached to the same carbon atom; in the one case, the bromine is eliminated, and a *p*-nitroaniline produced; in the other case, the chlorine is not eliminated, but some derivative of the iminoquinone type is formed. It is possible that the red substance above mentioned is such a derivative.

It is open to doubt whether, in the ordinary nitration of anilides, the stages observed in the action of nitric acid on these *s*-trihaloanilines actually occur; the nitroamino-derivatives of the anilides have never been obtained; it is possible that the nitrating agent reacts directly with an acyliminoquinone (compare Lapworth, *Trans.*, 1901, 79, 1267; Thiele, *Annalen*, 1899, 306, 87).

#### EXPERIMENTAL.

##### *Reaction of Nitric Acid with s-Tribromoaniline and the s-Dihaloanilines.*

*s-Tribromoaniline.*—Losanitsch (*loc. cit.*) heated *s*-tribromoaniline with nitric acid diluted with acetic acid and obtained 2:6-dibromo-4-nitroaniline, but he does not state the proportion of nitric acid used, or give the details of the experiment.

Five grams of the aniline were covered with 50 c.c. of glacial acetic acid (m. p. 15.2°) a quantity insufficient to completely dissolve this base at the ordinary temperature. To the solution containing some solid in suspension were added 7—8 c.c. of nitric acid (sp. gr. 1.5), which was colourless and free from nitrous acid\*; a crystalline precipitate of the aniline nitrate immediately separated. The mixture was

\* In the presence of nitrous acid, diazotisation took place to a large extent, confusing the direct interaction of the aniline and nitric acid.

now heated on the water-bath, when the nitrate dissolved, forming a solution which rapidly became deep orange, and then lighter in tint and more yellow than orange in colour. After about 20—30 minutes, the evolution of bromine had become very obvious, and on cooling 2:6-dibromo-4-nitroaniline (3·5 grams) separated in a nearly pure state. It melted at 205°; its acetyl derivative melted at 235°, and the acetylchloroamino-derivative at 109—110°; the last named contained Cl as :NCl = 9·33 per cent. (instead of 9·51 per cent.). A careful search was made in the mother liquors for 2:4-tribromo-6-nitroaniline, and for 2:4:6-tribromo-3-nitroaniline. The mother liquors were precipitated by water, and the solid thus obtained extracted with aqueous sodium carbonate (to remove any nitroamino-derivative), and then distilled in steam. The fact that the distillate was colourless indicated the absence of any *o*-nitroaniline (this vol., p. 496). Small amounts of *s*-tribromoaniline were alone found.

1-Nitroamino-2:4:6-tribromobenzene,  $C_6H_2Br_3 \cdot NH \cdot NO_2$ .—In order to isolate the nitroamine, the acetic acid solution at any time during the period of 5 to 15 minutes from the beginning of heating was poured on to ice; the yellow solid which separated was collected and washed free from acid. It was then extracted with cold dilute aqueous sodium carbonate. The remaining yellow solid, consisting mainly of unchanged *s*-tribromoaniline and 2:6-dibromo-4-nitroaniline, was filtered from the alkaline liquor, from which, on addition of a mineral acid, the nitroamine separated as a white precipitate. From 10 grams of aniline, 0·4 gram of nitroamine was obtained. It is readily soluble in all organic solvents except petroleum; from dilute acetic acid or dilute alcohol, it crystallises in flesh-coloured needles. In cold water, the nitroamine is insoluble; 1500 c.c. of hot water are required to dissolve 1 gram; from this solution, it crystallises in slender, long, often curved, flesh-coloured needles, melting and decomposing at 143—144° with evolution of oxides of nitrogen:

0·1634 gave 0·246 AgBr. Br = 64·04.

$C_6H_2O_2N_2Br_3$  requires Br = 63·98 per cent.

This substance is acid to litmus; on addition of aqueous sodium hydroxide to an aqueous solution of its sodium salt, the latter separates in pearly white plates:

0·3444 gave 0·053  $Na_2SO_4$ . Na = 5·62.

$C_6H_2O_2N_2Br_3Na$  requires Na = 5·79 per cent.

When the nitroamine is dissolved in acetic acid to which a drop of sulphuric acid has been added, the colour of the solution becomes orange, and after some time 2:6-dibromo-4-nitroaniline separates.

2-Chloro-4:6-dibromoaniline was treated in a perfectly similar



manner with nitric acid. 2-Chloro-6-bromo-4-nitroaniline was the main product; it melted at  $177^{\circ}$ , yielded an acetyl derivative melting at  $221^{\circ}$  and was in every respect identical with the synthetical product (this vol., p. 496). The nitroamine obtained in this case melted and decomposed at  $137^{\circ}$ ; as only a small quantity of the aniline was used, there was not sufficient of the nitroamine for analysis. From 2:6-dichloro-4-bromoaniline, 2:6-dichloro-4-nitroaniline (m. p.  $188^{\circ}$ ) was obtained; its acetyl derivative melted at  $210-211^{\circ}$ . The nitroamine was only obtained in very small quantity, and melted and decomposed at  $136-137^{\circ}$ .

*Reaction of Nitric Acid with s-Trichloroaniline and with s-Dihalogen-p-chloroanilines.*

*s-Trichloroaniline.*—Five grams of the aniline were dissolved in 50 c.c. of acetic acid and 8 c.c. of pure nitric acid added, whereupon the nitrate of the base immediately crystallised out. On heating the mixture on the water-bath, the solution became purple as the nitrate dissolved, and then rapidly changed to magenta, which more slowly became crimson. No chlorine was evolved. After 30 minutes' heating, a very small quantity (0.05 gram) of hexachloroazobenzene separated; on recrystallisation from chloroform and alcohol, it was obtained in long, lustrous, red needles, melting at  $188^{\circ}$ , identical in melting point, solubility, &c., with the specimen previously prepared by the action of acetylchloroamino-2:4-dichlorobenzene on s-trichloroaniline (Trans., 1901, 79, 467).

1-Nitroamino-2:4:6-trichlorobenzene,  $C_6H_2Cl_3 \cdot NH \cdot NO_2$ , was isolated in a manner completely similar to that used for the tribromo-derivative, and resembles the latter very closely in appearance and properties. It crystallises from much hot water in long, flesh-coloured needles, melting and decomposing at  $135^{\circ}$ :

0.1402 gave 14.2 c.c. of moist nitrogen at  $17^{\circ}$  and 775 mm.  $N = 11.93$ .  
0.1486 „ 0.266 AgCl.  $Cl = 44.26$ .

$C_6H_2O_2N_2Cl_3$  requires  $Cl = 44.06$ ;  $N = 11.63$  per cent.

Its sodium salt crystallises in glistening plates, and is very soluble in water or alcohol.

A solution in glacial acetic acid to which one drop of sulphuric acid has been added soon becomes crimson in colour. At the ordinary temperature, the nitroamine changes only slowly, but on heating on the water-bath it rapidly decomposes, the colour of the solution quickly deepening.

To isolate any substance or substances which may have been formed, the crimson solution obtained either from the nitroamine, or directly by

the action of nitric acid on an acetic acid solution of the aniline, was poured on to ice; the red solid was collected, washed free from acid, and extracted with aqueous sodium carbonate to remove any nitroamine. The solid was now fractionally crystallised from petroleum (b. p. 50–80°); finally, a small amount of a *substance* was obtained, which crystallised in elongated, brilliant red plates melting and decomposing at 143°, and very soluble in the usual solvents. It dissolved in concentrated sulphuric acid with a reddish-brown coloration; on addition of water and on warming, the solution became colourless. A solution in acetone was immediately reduced by zinc dust and acetic acid with the production of a colourless substance, crystallising in needles from petroleum melting at 188°. Sufficient of these substances (0.2 gram from 20 grams of aniline) could not be obtained by the above method for a complete investigation.

2:4-Dichloro-6-bromoaniline and 4-chloro-2:6-dibromoaniline behave in a completely analogous manner; from each, nitroamines were obtained, decomposing at nearly the same temperature, 137–138°. Azobenzenes were formed in small amount. From the red solutions, obtained as in the case of *s*-trichloroaniline, no attempt was made to isolate the corresponding red substances.

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## LI.—Some *s*-Chlorobromonitroanilines and their Derivatives.

By K. J. P. ORTON.

FOR the purpose of recognising the products possibly obtainable by the action of nitric acid on the *s*-trihalogenanilines (see preceding communication), the anilines hereafter described were prepared and their derivatives investigated.

As in the case of all di-*o*-substituted anilines, monoacetyl derivatives are only with difficulty prepared from these bases—a difficulty which is intensified if a nitro-group occupies one ortho-position. Only after many hours' heating with excess of acetyl chloride and sodium acetate is the acetyl derivative obtained. When quite free from the respective bases, the monoacetyl derivatives of the anilines possessing a nitro-group either in the ortho- or the para-position (for example, 2:4-dibromo-6-nitro- and 2:6-dibromo-4-nitro-anilines) are quite colourless; but when obtained from the aniline as just mentioned, even after

repeated recrystallisation, they are generally of a yellow tint owing to the presence of traces of the latter.

All di-*o*-halogen acetanilides (as *s*-tribromoacetanilide) dissolve fairly readily in 10 per cent. aqueous sodium hydroxide, and are precipitated unchanged by acids; these alkaline solutions may be heated for a considerable time without effecting any appreciable hydrolysis.

The acetyl derivatives of *s*-trisubstituted anilines, with a nitro-group in an ortho- or a para-position, dissolve readily even in *N*/10 cold aqueous sodium hydroxide; the anilides with an *o*-nitro-group form an orange-coloured solution, which becomes markedly redder on warming; those with a *p*-nitro-group form a canary-yellow solution which does not much deepen in tint when warmed. From these alkaline solutions, acids precipitate the anilides as perfectly white solids. By taking advantage of the solubility of the anilides, they may be obtained completely free from the anilines after acetylation. Although these *s*-trisubstituted nitroanilides are more difficultly hydrolysed than even di-*o*-halogen anilides (*s*-tribromoacetanilide, &c.) by boiling with sulphuric or hydrochloric acid and alcohol, they are very easily converted into anilines when their solutions in excess of 10 per cent. aqueous sodium hydroxide are heated for a short time (compare Kleemann, *Ber.*, 1888, 19, 336).

The diacetyl derivatives of *s*-trisubstituted anilines are formed when the aniline is boiled or heated under pressure with acetic anhydride for some hours. In this operation, no formation of monoacetylated compound takes place, although some of the aniline frequently remains unchanged, when the heating has not been sufficiently prolonged. The diacetanilides are very rapidly converted into the monoacetyl derivatives by aqueous alkalis.

To recognise a small amount of an *o*-nitrodihalogen aniline in the presence of a much larger quantity of the para-isomeride, it is best to distil the mixture in steam. Although both anilines pass over, the ortho-isomeride distils more readily and gives a canary-yellow distillate, whilst the para-derivative gives a colourless distillate. By this means, not only can the presence of the ortho-compound be recognised easily in a mixture containing less than 2 per cent., but 0.02 gram can be readily detected.

#### EXPERIMENTAL.

*2-Chloro-6-bromo-4-nitroaniline*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{ClBr} \cdot \text{NH}_2$ , was prepared from 2-bromo-4-nitroaniline; the latter was obtained by adding a solution of bromine (1 mol.) in glacial acetic acid to a hot solution of *p*-nitroaniline (1 mol.) in the same solvent. On cooling, a little 2:6-dibromo-4-nitroaniline separates. The acetic acid solution was

precipitated by water, and the mixture of anilines thus obtained dissolved in alcohol, to which was added a weight of sulphuric acid equal to that of the *p*-nitroaniline used. On now adding water, only 2-bromo-4-nitroaniline separates, whilst any *p*-nitroaniline remains dissolved in the acid. The yield is about 75 per cent. of the calculated amount.

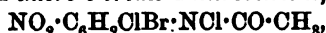
2-Bromo-4-nitroaniline was chlorinated by passing dry chlorine into its solution in dry benzene; chlorination is completed when the solid which separates settles easily to the bottom of the flask. This solid, which is the hydrochloride of 2-chloro-6-bromo-4-nitroaniline, was collected and well washed with petroleum. On digesting it with water, the aniline is obtained. The latter is only slightly soluble in all solvents, and crystallises from alcohol in long, prismatic, bright yellow needles melting at 177°:

0.2636 gave 0.345 AgCl + AgBr and 0.2248 Ag. Cl = 14.02; Br = 31.58.  
 $C_6H_4O_2N_2ClBr$  requires Cl = 14.09; Br = 31.78 per cent.

2-Chloro-6-bromo-4-nitroacetanilide,  $NO_2 \cdot C_6H_2ClBr \cdot NH \cdot CO \cdot CH_3$ , was prepared by adding acetyl chloride in some excess to a warm solution of the aniline in glacial acetic acid. The mixture was then boiled for half-an-hour. From alcohol, in which it is only slightly soluble, the anilide separates in lustrous, white prisms melting at 221—222°:

0.1916 gave 0.2163 AgCl + AgBr and 0.1406 Ag. Cl = 11.86; Br = 27.66.  
 $C_8H_6O_2N_2ClBr$  requires Cl = 12.08; Br = 27.24 per cent.

Acetylchloroamino-2-chloro-6-bromo-4-nitrobenzene,



prepared from the anilide in the manner previously described, crystallises in white, lustrous prisms, melting at 84—85°:

0.1727 liberated I = 10.5 c.c. *N*/10 iodine. Cl as :NCl = 10.77.

$C_8H_5O_2N_2Cl_2Br$  requires Cl as :NCl = 10.81 per cent.

2-Chloro-6-bromo-4-nitrodiacetanilide,  $NO_2 \cdot C_6H_2ClBr \cdot N(CO \cdot CH_3)_2$ , was prepared by boiling the aniline (1 gram) with acetic anhydride (10 grams) for 10 hours; some unchanged aniline still remained. The diacetyl derivative was readily soluble in all solvents, and crystallised from petroleum in long, four-sided, white prisms melting at 133—133.5°. It was not analysed.

2-Chloro-4-bromo-6-nitroaniline,  $NO_2 \cdot C_6H_2ClBr \cdot NH_2$ , was prepared from the anilide; the latter (2 grams) was dissolved in 20 c.c. of a 10 per cent. solution of sodium hydroxide; the solution was then heated on the water-bath; after 10 minutes, the aniline began to separate, and hydrolysis was complete in half-an-hour. The aniline was crystallised from alcohol, in which it is far more soluble than

the isomeride just described. It forms silky, yellow needles melting at  $114^{\circ}$ :

0.1850 gave 0.2432 AgCl + AgBr and 0.1584 Ag. Cl = 14.01; Br = 31.84.

$C_6H_4O_2N_2ClBr$  requires Cl = 14.09; Br = 31.78 per cent.

*2-Chloro-4-bromo-6-nitroacetanilide*,  $NO_2 \cdot C_6H_2ClBr \cdot NH \cdot CO \cdot CH_3$ , was prepared from 2-chloro-4-bromoacetanilide; the latter (10 grams) was added in small portions to 50 c.c. of ice-cold nitric acid (sp. gr. 1.5). The acid solution was thrown on to ice, and the solid which separated recrystallised from alcohol. The anilide crystallises in white needles or prisms melting at  $194^{\circ}$ :

0.1306 gave 0.1466 AgCl + AgBr and 0.0956 Ag. Cl = 12.07; Br = 26.96.

$C_8H_6O_3N_2ClBr$  requires Cl = 12.08; Br = 27.24 per cent.

*Acetylchloroamino-2-chloro-4-bromo-6-nitrobenzene*,

$NO_2 \cdot C_6H_3ClBr \cdot NCl \cdot CO \cdot CH_3$ ,

was prepared in the usual way from the anilide. It crystallises in long, pale yellow, lustrous prisms melting at  $56-57^{\circ}$ :

0.1706 liberated I = 10.6 c.c. *N*/10 iodine. Cl as :NCl = 11.02.

$C_8H_5O_3N_2Cl_2Br$  requires Cl as :NCl = 10.81 per cent.

This substance is readily soluble in petroleum. It is noteworthy that this chloroamino-derivative is yellow, although obtained from a colourless anilide; in its low melting point it differs from the chloroamines of other di-*o*-substituted anilides.

*4-Chloro-2-bromo-6-nitroaniline*,  $NO_2 \cdot C_6H_2ClBr \cdot NH_2$ , was prepared by hydrolysing the anilide in the manner just described. It crystallises from alcohol in yellow, silky needles melting at  $114-115^{\circ}$ :

0.1428 gave 0.1876 AgCl + AgBr and 0.1224 Ag. Cl = 14.14; Br = 31.52.

$C_6H_4O_2N_2ClBr$  requires Cl = 14.09; Br = 31.78 per cent.

*4-Chloro-2-bromo-6-nitroacetanilide*,  $NO_2 \cdot C_6H_2ClBr \cdot NH \cdot CO \cdot CH_3$ , was prepared by nitrating 4-chloro-2-bromoacetanilide. It crystallises from alcohol in colourless needles or flattened prisms melting at  $207^{\circ}$ :

0.1824 gave 0.2048 AgCl + AgBr and 0.1338 Ag. Cl = 12.29; Br = 26.65.

$C_8H_5O_3N_2ClBr$  requires Cl = 12.08; Br = 27.24 per cent.

*Acetylchloroamino-2:6-dibromo-4-nitrobenzene*,

$NO_2 \cdot C_6H_2Br_2 \cdot NCl \cdot CO \cdot CH_3$ .

This hitherto undescribed chloroamine was prepared from the anilide. It crystallises from petroleum (b. p.  $50-80^{\circ}$ ) in small, four-sided prisms with domed ends, melting at  $110-111^{\circ}$ :

0.488 liberated I = 25.5 c.c. *N*/10 iodine. Cl as :NCl = 9.27.

$C_8H_3O_3N_2ClBr_2$  requires Cl as :NCl = 9.51 per cent.

**2:4-Dibromo-6-nitrodiacetanilide**,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{N}(\text{CO} \cdot \text{CH}_3)_2$ , was prepared by boiling the aniline (1 gram) with acetic anhydride (10 grams) for several hours. After evaporation of the excess of acetic anhydride, the solid residue was recrystallised from petroleum. It forms aggregates of colourless, rhombic prisms melting at  $96-97^\circ$ :

0.1847 gave 0.1840 AgBr. Br = 42.39.

$\text{C}_{10}\text{H}_8\text{O}_4\text{N}_2\text{Br}_2$  requires Br = 42.07 per cent.

**2:3:4:6-Tetrabromoacetanilide**,  $\text{C}_6\text{HBr}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_3$ , was prepared by acetylating the aniline with acetyl chloride in the manner above described. It crystallises from benzene in silky needles melting at  $228-229^\circ$ , and is fairly soluble in alcohol and acetic acid:

0.1762 gave 0.2784 AgBr. Br = 67.22.

$\text{C}_6\text{H}_3\text{ONBr}_4$  requires Br = 67.35 per cent.

**2:3:4:6-Tetrabromodiacetanilide**,  $\text{C}_6\text{HBr}_4 \cdot \text{N}(\text{CO} \cdot \text{CH}_3)_2$ , prepared in the usual way from the aniline and acetic anhydride, crystallises from petroleum in transparent, four-sided prisms melting at  $164^\circ$ , and is very soluble in all solvents except petroleum (b. p.  $50-80^\circ$ ):

0.11 gave 0.1674 AgBr. Br = 64.76.

$\text{C}_{10}\text{H}_7\text{O}_2\text{NBr}_4$  requires Br = 64.88 per cent.

**2:3:6-Tribromo-4-nitroaniline**,  $\text{NO}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{NH}_2$ .—This aniline was prepared from 3-bromo-4-nitroaniline (m. p.  $170^\circ$ ), by the action of bromine on an acetic acid solution of the latter. It crystallises from alcohol, in which it is only slightly soluble when cold, in pale lemon-yellow needles melting at  $155-155.5^\circ$ :

0.1775 gave 0.2672 AgBr. Br = 64.04.

$\text{C}_6\text{H}_3\text{O}_2\text{N}_2\text{Br}_3$  requires Br = 63.98.

This aniline distils slowly in steam, and as in the case of other *p*-nitroanilines, the aqueous distillate is colourless, whilst the distillate of the isomeric *o*-nitroaniline is bright yellow.

**2:3:4-Tribromo-6-nitroaniline**,  $\text{NO}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{NH}_2$ , prepared from 3-bromo-6-nitroaniline (m. p.  $151^\circ$ ), crystallises in orange-yellow needles melting at  $165.5-166^\circ$ :

0.1266 gave 0.1908 AgBr. Br = 64.12.

$\text{C}_6\text{H}_3\text{O}_2\text{N}_2\text{Br}_3$  requires Br = 63.98 per cent.

The acetyl derivative crystallises in flattened, white needles melting at  $221^\circ$ .

The 3-bromo-4-nitro- and the 3-bromo-6-nitro-anilines just mentioned were prepared by nitrating *m*-bromoaniline. *m*-Bromoaniline (1 part) was dissolved in concentrated sulphuric acid (10 parts), and to the ice-cold solution the calculated quantity of nitric acid (sp. gr.

1.5) dissolved in sulphuric acid was added. The acid solution was poured on to ice, and the nitroanilines precipitated with ammonia. They are separated by distilling in steam from an equal weight of sulphuric acid; 3-bromo-6-nitroaniline distils over whilst 3-bromo-4-nitroaniline remains in the distilling flask. After one recrystallisation from alcohol, each possesses the correct melting point (compare Claus and Scheulen, *J. pr. Chem.*, 1891, [ii], 43, 201; Claus and Wallbaum, *ibid.*, 1897, [ii], 56, 54).

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## LII.—*The Nitration of s-Trihalogen Acetanilides.*

By K. J. P. ORTON.

IN a previous paper (this vol., p. 490), it was shown that in the action of nitric acid on the *s*-trihalogen anilines (*s*-tribromoaniline, &c.), a bromine atom in the para-position relatively to the amino-group was replaced by a nitro-group, whilst this is not the case with a *p*-chlorine atom or an *o*-bromine atom (at least, under the same conditions). Further, it appeared very probable that at least one intermediate product, a nitroamine, existed between the nitrate of the aniline first formed and the final product (or products). It seemed desirable to ascertain what action nitric acid had on the acetyl derivatives of the *s*-trihalogen anilines, and whether, in this case also, a *p*-bromine atom was displaced.

The action of nitric acid on *s*-tribromoacetanilide has been studied by Remmers (*Ber.*, 1874, 7, 351), who obtained an anilide which is described as crystallising in yellow needles readily soluble in alcohol; no melting point of the compound is given, and the numbers found in an estimation of bromine correspond with those required for the formula  $\text{NO}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_3$ . By hydrolysis with ammonia, an aniline was obtained from it which crystallised in insoluble, yellow needles melting at 214–215°; a bromine determination indicated that the aniline was represented by the formula  $\text{NO}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{NH}_2$ . This substance could not be 2 : 4 : 6-tribromo-3-nitroaniline, which was prepared by Körner (*Jahresber.*, 1875, 347) from *m*-nitroaniline and melts at 102.5°. It was possible in Remmers' experiments that the nitro-group had displaced a bromine atom either from the ortho- or the para-position, the liberated bromine entering the aniline molecule in the meta-position. This transformation, sufficiently improbable in itself, does not produce either 2 : 3 : 6-tribromo-4-nitroaniline or 2 : 3 : 4-tri-

bromo-6-nitroaniline, which, the author has shown, melt respectively at 155° and 166° (this vol., p. 499). The other possible aniline has not hitherto been described.\*

Bentley (*Amer. Chem. J.*, 1898, 20, 472) repeated Remmers' experiments, but was unable to obtain any evidence of the substance, described by him, and only succeeded in isolating the final products of the action of nitric acid on this anilide, such as bromoanil, &c.

I have therefore reinvestigated the action of nitric acid on *s*-tribromoacetanilide. When diluted with acetic acid, nitric acid has little or no action on this substance; when dissolved in cold fuming nitric acid (sp. gr. 1.5), the anilide is only slowly attacked, but when this solution in nitric acid is kept at a temperature of 50—55° for 15 minutes, the compound is largely converted into 2:4:6-tribromo-3-nitroacetanilide. No bromine is evolved and no other substances are produced.

Under similar treatment, 4-chloro-2:6-dibromoacetanilide yields 4-chloro-2:6-dibromo-3-nitroacetanilide. Both these anilides have been converted into the corresponding anilines, namely, 2:4:6-tribromo-3-nitroaniline and the hitherto undescribed 4-chloro-2:6-dibromo-3-nitroaniline. These bases have also been prepared respectively from *m*-nitroaniline and 4-chloro-3-nitroaniline, and a comparison has been made of the anilines and their acetyl and acetylchloro-amino-derivatives obtained from both sources.

It would appear from these results that the acetyl derivatives of these *s*-trihalogen anilines behave, with nitric acid, in a manner initially different from the *s*-trihalogen anilines themselves; there is not only no sign of the formation of nitroamino-derivatives and of the products of their transformation, namely, replacement of the *p*-bromine atom, but there is also no indication that the nitric acid reacts with an iminoquinone derivative, as suggested in the previous communication, in which case the *p*-bromine atom would probably also be eliminated. The directing influence of the amino-group as thus defined has been at least partially suppressed on acetylation (compare Armstrong and Horton, *Proc.*, 1901, 17, 246). An analogous case is the nitration of aniline sulphates in the meta-position relatively to the amino-group in the presence of a large quantity of sulphuric acid (Nölting and Collin, *Ber.*, 1884, 17, 226). The behaviour of *s*-tribromophenol towards nitric acid may be quoted to illustrate a similar phenomenon when an oxygen, instead of a nitrogen, atom is the directing agent in substitution; this phenol yields 2:6-dibromo-4-nitrophenol (Armstrong and Harrow, *Trans.*, 1876, 30, 477), the *p*-bromine atom being replaced by

\* As Remmers obtained his substituted aniline (m. p. 214—215°) by heating the anilide under pressure with ammonia, it is possible that a profound change took place, and not a simple hydrolysis.



a nitro-group, whereas the ethyl ether, 1-ethoxy-2:4:6-tribromobenzene yields 1-ethoxy-2:4:6-tribromo-3-nitrobenzene (compare Guareschi and Dacomo, *Ber.*, 1885, 18, 1175, and Faust, *Annalen*, 1869, 149, 152).

#### EXPERIMENTAL.

##### *Nitration of $\alpha$ -Tribromoacetanilide.*

Five grams of  $\alpha$ -tribromoacetanilide (m. p.  $233^{\circ}$ ) were added to 5 c.c. of fuming nitric acid; the anilide rapidly dissolves, and the solution is cautiously warmed to about  $55^{\circ}$  for 15 minutes. It is then poured on to ice; the nearly colourless solid which separates is washed free from acid and dried. It is readily soluble in alcohol (compare Remmers, *loc. cit.*), and dissolves in a 10 per cent. solution of sodium hydroxide, forming a colourless solution, whereas a nitroacetanilide, in which the nitro-group is either in an ortho- or the para-position, dissolves in sodium hydroxide with a marked yellow coloration (this vol., p. 496). Recrystallised from benzene or dilute acetone, it forms colourless plates melting at  $197^{\circ}$ , and, after repeated fractional crystallisation, at  $203^{\circ}$ . An analysis of this product gave numbers which indicated that it was a mixture of  $\alpha$ -tribromoacetanilide and a tribromonitroacetanilide.

It was found that these two anilides could be separated from the mixture (m. p.  $197^{\circ}$ ) by converting them into the chloroamino-derivatives. The mixture was dissolved in warm glacial acetic acid and some excess of a solution of bleaching powder (0.8 normal,  $\text{HClO}$ ) was added. The oil which at first separated solidified on cooling; the solid was dried on a porous tile and then dissolved in a boiling mixture of chloroform and petroleum. On cooling, crystals separated which melted at  $148^{\circ}$ ; on recrystallisation from petroleum (b. p.  $50-80^{\circ}$ ), an acetylchloroamino-derivative separated in characteristic translucent, lustrous prisms melting at  $159^{\circ}$ , which is the melting point of acetylchloroamino-2:4:6-tribromo-3-nitrobenzene (see below):

0.1485 liberated  $\text{I} = 6.4$  c.c.  $\text{N}/10$  iodine.  $\text{Cl}$  as  $\text{NCl} = 7.64$ .

$\text{NO}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{NCl} \cdot \text{CO} \cdot \text{CH}_3$  requires  $\text{Cl}$  as  $\text{NCl} = 7.85$  per cent.

From the first mother liquor (a mixture of chloroform and petroleum), impure acetylchloroamino-2:4:6-tribromobenzene (m. p.  $100^{\circ}$  instead of  $110^{\circ}$ ) was obtained; by treatment with alcohol, this was converted into  $\alpha$ -tribromoacetanilide.

From the acetylchloroamino-2:4:6-tribromo-3-nitrobenzene (m. p.  $159^{\circ}$ ), the corresponding anilide, 2:4:6-tribromo-3-nitroacetanilide, was prepared by the action of warm alcohol; it crystallised from dilute acetone in tufts of silky needles melting at  $217^{\circ}$ :

0.2012 gave 12.2 c.c. moist nitrogen at  $15^{\circ}$  and 761 mm.  $\text{N} = 6.93$ .

$\text{C}_8\text{H}_5\text{O}_3\text{N}_2\text{Br}_3$  requires  $\text{N} = 6.73$  per cent.

The corresponding base, 2:4:6-tribromo-3-nitroaniline, was obtained by heating the anilide (1 part) with sulphuric acid (4 parts) and alcohol (4 parts) for several hours. On adding water, the aniline separated and crystallised from dilute alcohol in small, pale yellow needles melting at 102° (Körner, *loc. cit.*, gives 102.5°).

This base was also prepared from *m*-nitroaniline; from this specimen, on boiling with acetyl chloride in the presence of glacial acetic acid, 2:4:6-tribromo-3-nitroacetanilide,  $\text{NO}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_3$ , was obtained, which crystallised in needles from dilute acetone, and in flattened prisms or plates from benzene, and melted at 216—217°:

0.148 gave 0.2004 AgBr. Br = 57.59.

$\text{C}_8\text{H}_5\text{O}_3\text{N}_2\text{Br}_3$  requires Br = 57.54 per cent.

2:4:6-Tribromo-3-nitrodiaacetanilide,  $\text{NO}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{N}(\text{CO} \cdot \text{OH})_2$ .—The base or its monoacetyl derivative (1 gram) was boiled with acetic anhydride (8 grams) for six hours. The anhydride was evaporated on the water-bath, and the solid residue dissolved in chloroform. Large lustrous, perfectly transparent rhombs separated melting at 175—176°; these were readily soluble in alcohol, less so in acetic acid, and only slightly so in cold benzene or chloroform:

0.158 gave 0.1946 AgBr. Br = 52.4.

$\text{C}_{10}\text{H}_7\text{O}_4\text{N}_2\text{Br}_3$  requires Br = 52.28 per cent.

*Acetylchloroamino*-2:4:6-tribromo-3-nitrobenzene,



prepared from the anilide, crystallised in lustrous prisms from a mixture of chloroform and petroleum and melted at 159°:

0.366 liberated I = 15.6 c.c. *N*/10 iodine. Cl as :NCl = 7.55.

$\text{C}_8\text{H}_4\text{O}_3\text{N}_2\text{ClBr}_3$  requires Cl as :NCl = 7.85 per cent.

*Nitration of 4-Chloro-2:6-dibromoacetanilide.*—The nitration of this anilide was carried out in a manner exactly similar to that employed in the case of *s*-tribromoacetanilide. The mixture of unchanged anilide and nitrated product melted at 191°; it was dissolved in glacial acetic acid and treated with a solution of bleaching powder; the chloroamines thus obtained were dissolved in a hot mixture of chloroform and petroleum, and from the solution crystals separated which melted at 125—130°. These were recrystallised from petroleum. Pure *acetylchloroamino-4-chloro-2:6-dibromo-3-nitrobenzene*,



separated in aggregates of short prisms which melted at 134—135°:

0.1973 liberated I = 10.0 c.c. *N*/10 iodine. Cl as :NCl = 8.98.

$\text{C}_8\text{H}_4\text{O}_3\text{N}_2\text{Cl}_2\text{Br}_2$  requires Cl as :NCl = 8.71 per cent.

From the first mother liquor, a mixture of chloroform and petroleum, impure acetylchloroamino-4-chloro-2:6-dibromobenzene (m. p.  $102^{\circ}$  instead of  $110^{\circ}$ ) was obtained which was reconverted into the anilide; after recrystallisation, the latter melted at  $226^{\circ}$ .

*4-Chloro-2:6-dibromo-3-nitroacetanilide*,  $\text{NO}_2 \cdot \text{C}_6\text{HClBr}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_3$ .—This anilide was prepared by acetylating 4-chloro-2:6-dibromo-3-nitroaniline with acetyl chloride. It crystallised from dilute alcohol in tufts of silky needles melting at  $224^{\circ}$ , and was moderately soluble in alcohol, acetic acid, or benzene:

0.1442 gave 0.201 AgCl + AgBr and 0.1253 Ag. Cl = 9.49; Br = 42.99.

$\text{C}_8\text{H}_5\text{O}_2\text{N}_2\text{ClBr}_2$  requires Cl = 9.52; Br = 42.93 per cent.

It was also obtained from the corresponding chloroamine, prepared from the product of nitration of 4-chloro-2:6-dibromoacetanilide. This specimen crystallised in silky needles melting at  $224^{\circ}$ :

0.2022 gave 13.9 c.c. of moist nitrogen at  $17.2^{\circ}$  and 763 mm. N = 7.80.

$\text{C}_8\text{H}_5\text{O}_2\text{N}_2\text{ClBr}_2$  requires N = 7.54 per cent.

*4-Chloro-2:6-dibromo-3-nitroaniline*,  $\text{NO}_2 \cdot \text{C}_6\text{HClBr}_2 \cdot \text{NH}_2$ , was prepared by brominating 4-chloro-3-nitroaniline (m. p.  $103$ – $104^{\circ}$ ), and it was also obtained by hydrolysis of the product of nitration of 4-chloro-2:6-dibromoacetanilide. It crystallises in small, pale yellow needles melting at  $103^{\circ}$ , and is fairly soluble in all the usual organic solvents:

0.140 gave 0.2195 AgCl + AgBr and 0.1368 Ag. Cl = 10.73; Br = 48.39.

$\text{C}_8\text{H}_5\text{O}_2\text{N}_2\text{ClBr}_2$  requires Cl = 10.62; Br = 48.43 per cent.

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### LIII.—*Preparation of Sulphamide from Ammonium Amidosulphite.*

By EDWARD DIVERS and MASATAKA OGAWA.

SULPHAMIDE occurs among the products of the spontaneous decomposition of ammonium amidosulphite. That this appeared to be the case was mentioned in the paper describing this salt (Trans., 1900, 77, 324). It had then been isolated, not only in too small a quantity to admit of its purification and full analysis, but in a way that rendered its identity almost doubtful. The decomposed amidosulphite had been extracted with 95 per cent. alcohol, the residue from the evaporated voluminous

solution extracted with undried ether, and the again very voluminous solution evaporated. Half a gram of crystalline residue from about 150 c.c. of the ether solution was thus obtained, answering the tests for sulphamide, but melting much above  $81^{\circ}$ , tasting not bitter, and yielding a little too much sulphur on analysis. Then, too, we had failed to get silver sulphamide from the aqueous solution of the decomposed amidosulphite, owing, as we afterwards found, to our having used ammonia in excess. All these points differed, or seemed to differ, from Traube's description, and caused us to hesitate in pronouncing the substance to be sulphamide. Since then we have obtained it in larger quantity and pure, and thus become certain that sulphamide is a little soluble in absolute alcohol and even very slightly so in dry ether, that it melts at  $91^{\circ}$ , and that its silver derivative is insoluble in ammonia alone, but soluble in ammonia in presence of the ammonium nitrate which its mother liquor always contains. The publication of Hantzsch and Holl's important contribution to the knowledge of sulphimide and sulphamide (*Ber.*, 1901, 34, 30), in which Traube's account of sulphamide (*Ber.*, 1893, 26, 609) is amended, affords welcome confirmation, so far as it goes, of the correctness of our own observations.

Hitherto, as is well known, sulphamide has only been got from sulphuryl chloride and ammonia, a mode of preparing it which Hantzsch and Holl have shown to be most laborious and unprofitable, and the difficulty of getting it in this way has quite recently induced Ephraim to try to obtain it from sulphuryl chloride by means of urethane, but without success (*Ber.*, 1902, 35, 776). Sulphuryl chloride is stated to give only 1—2 per cent. of pure sulphamide, whilst ammonium amidosulphite, by a process not unduly troublesome, yields 10 per cent. of its weight, and probably much more by skill and care.

In order to prepare the ammonium amidosulphite and decompose it afterwards, ammonia in excess and sulphur dioxide are led into a closed flask, fitted with a thermometer and an exit-tube dipping in mercury. To absorb the heat caused by the combination of the gases, the flask is held in a bath of brine and crushed ice, which is more effective when the flask contains some ether and is kept in motion, because then the salt does not stick to the walls of the flask as a waxy, badly-conducting coating. The rate of flow of the gases is to be regulated by the operator's ability to prevent the temperature in the flask from rising much above  $10^{\circ}$ . The inside of the apparatus, the gases, and the ether are all to be dried before use.

When as much amidosulphite has been formed as may be wanted or be convenient to prepare, the cooling mixture in the bath is replaced by water, and a slow stream of dry hydrogen passed through the flask, whilst the temperature of the water is slowly raised to about  $70^{\circ}$  and then kept at that point for five or six hours or so long as ammonia

continues to come off in any quantity. During this operation, the ether, if used, also evaporates. The sulphamide is all formed at temperatures not higher than 30—35°, and a higher temperature is here employed only for the purpose of destroying as much as possible of the thionic compounds which are formed along with the sulphamide and would at a later stage consume much silver nitrate and undesirably produce much ammonium nitrate, if present. The employment of a higher temperature than 70° to destroy all the thionic compounds, is not possible, because then the sulphamide itself would be decomposed.

When the flask has cooled down, enough ice-cold water is poured in to dissolve all its contents other than the considerable quantity of sulphur left by the destroyed compounds. To the yellow, unfiltered solution, which has been poured into an open vessel, barium hydroxide is added in quantity a little more than sufficient for the salts it precipitates, among which are sulphate, imidosulphite, and thiosulphate. In order to lessen the dilution of the solution of sulphamide, the barium hydroxide is used in mixed solution and crystals, as obtained by rapidly cooling a hot, concentrated solution. The precipitate is to be filtered off, although it is not very easy to get a bright filtrate, and, even when this is accomplished, the filtrate soon becomes turbid again, owing to further production of sulphate by the decomposing salts present in it. This does not matter, however, and to the turbid filtrate silver nitrate is added just so long as it continues to give a precipitate. The barium hydroxide will have liberated much ammonia, but a good deal of this will have evaporated during the time taken up in filtration, especially if the precipitation has been carried out in an open vessel. What remains of it, interferes only temporarily with the silver precipitation, and does not usually need external neutralisation, for so much acid is formed as the result of a very rapid decomposition of the precipitated silver salts (in which they change from white to black) as to be more than enough to neutralise the ammonia remaining in the solution, and also to dissolve up any silver sulphamide that may have been thrown down at first. When the mother liquor has become thoroughly acid or, exceptionally, has been made so by adding nitric acid, and still holds silver in solution, it is filtered from the black precipitate and just neutralised with ammonia. Any slight precipitate then formed is also filtered off and rejected; it contains no trisulphimide. The filtrate holds little else than sulphamide and ammonium amidosulphate, and if evaporated over sulphuric acid would yield both these substances in characteristic crystals. But to isolate the sulphamide, it is to be precipitated from this solution by silver nitrate and ammonia, that is, by Traube's method. The silver sulphamide, thus obtained, is almost pure, there being no such acid matter present as is met with when the sulphamide has been prepared

from sulphuryl chloride. In that case, a viscid silver salt accompanies the silver sulphamide, and according to Hantzsch and Holl, can only be removed from it by a process entailing the destruction of much of the sulphamide. Even in the present case, however, the amidosulphate left with the sulphamide may cause a little difficulty, unless care be taken.

On referring to the memoir on amidosulphuric acid in the Transactions of the Society for 1896 (pp. 1647—1649, "amidosulphonic acid"), it will be found there stated that when an alkali is added in suitable quantity to a solution of mixed silver nitrate and potassium amidosulphate, a bright yellow, amorphous salt is precipitated, which is very probably  $\text{AgHN}\cdot\text{SO}_3\text{K}$ , and is soluble in, and ultimately decomposed by, excess of alkali. It is now found that, in precipitating silver sulphamide in presence of ammonium amidosulphate, as in the present case, a very small quantity of a bright yellow substance, probably ammonium argentamidosulphate, is apt to accompany the silver sulphamide, and that in order to circumvent this liability and at the same time to avoid loss of the silver sulphamide through its solubility in ammonia in presence of ammonium nitrate, precipitation should be carried out in the following way. Having added more silver nitrate, dilute ammonia is dropped in, slowly and with stirring, until the solution is slightly alkaline. The precipitate is quickly filtered off and washed free from mother liquor. The solution is again treated with silver nitrate and ammonia, as before, in order to see whether any more sulphamide is thrown down. This being quickly filtered off, if it be desired to obtain a sight of the yellow compound, a few drops or more of ammonia may be added, and dilute silver nitrate very slowly dropped in, when it will be produced.

The silver sulphamide, perhaps a little yellow after all, is to be dissolved in dilute nitric acid, ammonia added to slight alkalinity, as before, and then two or three drops of silver nitrate. After a repetition of this treatment, the precipitate is treated with exactly enough dilute hydrochloric acid to decompose it, just as Traube directs. The filtrate from the silver chloride, which must not be acid, gives the sulphamide in good crystals, when it is evaporated in the desiccator. It is to be recrystallised. Since it is exceedingly soluble, the mother-liquors must be worked up, if a good yield is wanted.

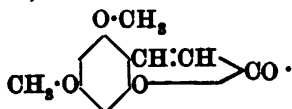
We are under obligations to Mr. Tojiro Suzuki for material assistance in the experimental work of this paper.

LIV.—*The Constitution of Limettin.*

By W. A. TILDEN and H. BURROWS.

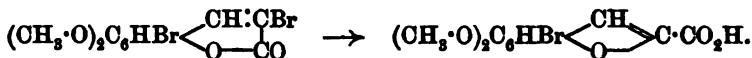
LIMETTIN is a substance which occurs in the pericarp of the lime fruit and is deposited from the essential oil which has been extracted by the sponge process or by pressure. It was shown by Tilden (*Trans.*, 1892, 61, 344) that its composition is expressed by the molecular formula  $C_{11}H_{10}O_4$ , and its constitution by the formula  $C_6H_3(O\cdot CH_2)_2\cdot C_3HO_2$ . The same substance has been since shown by E. Schmidt (*Apoth. Zeit.*, 1901, 16, 619) to be present in oil of lemon, and this observation is confirmed by the experiments of Burgess (*Proc.*, 1901, 17, 171).

From what follows, it appears that the constitution of limettin is similar to that of coumarin, and that the group  $C_3HO_2$  has the structure of an unsaturated lactone ring, corresponding to that of coumarin. Limettin is, in fact, 4:6-dimethoxycoumarin, isomeric with dimethoxy-scouletin and daphnetin,



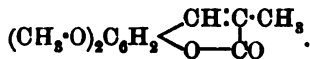
This view of its constitution is supported by the facts, recorded in the previous paper, that limettin is soluble in strong alkali solutions and is reprecipitated unchanged by acids, and that the products of fusion with potash are phloroglucinol and acetic acid.

The dibromo-derivative, when treated with alkali, readily yields up one atom of bromine in the formation of the corresponding monobrominated coumarilic acid,



Di- and tri-chlorolimettin behave in a similar manner.

Owing to its extreme solubility, the sodium salt of limettin cannot be isolated from its aqueous solution, but it is precipitated by the use of an alcoholic solution of sodium ethoxide. This compound could not be methylated by the action of methyl iodide, unchanged limettin being the only product. From the corresponding silver salt, however, a small quantity of a homologue was formed, together with a relatively large proportion of limettin. From considerations which appear later, the homologue has the following structure:



An attempt was made to synthesise limettin by proceeding from the aldehyde from phloroglucinol, described by Gattermann and Köbner (*Ber.*, 1899, 32, 280), by condensation with acetic anhydride, but it was found that under the conditions tried the saponified product was unchanged by the action of methyl iodide.

#### EXPERIMENTAL.

The material required in the following experiments was prepared from the same source as the original specimen, namely, the deposit which is filtered from commercial oil of limes. As described in the first paper (*loc. cit.*), it melts at 145° and exhibits a distinct blue fluorescence, but was never obtained perfectly white.

#### *Bromo-4 : 6-dimethoxycoumarilic Acid.*

Dibromolimettin, boiled with a 10 per cent. solution of aqueous potash, readily dissolved, and the solution, after cooling, gave a copious precipitate when acidified. The substance, recrystallised from acetic acid, exhibited acid properties and melted at 239°.

Dibromocoumarin, when similarly treated, behaves in exactly the same way, and yields monobromocoumarilic acid.

Representing dibromolimettin by the formula



the corresponding coumarilic acid is  $(\text{CH}_3\cdot\text{O})_2\text{C}_6\text{HBr} \begin{array}{c} \text{CH} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{C}\cdot\text{CO}_2\text{H} \end{array}$  :

0.3052 gave 0.4900 CO<sub>2</sub> and 0.0786 H<sub>2</sub>O. C = 43.79; H = 2.86.

0.3396 „ 0.2100 AgBr. Br = 26.31.

C<sub>11</sub>H<sub>9</sub>O<sub>5</sub>Br requires C = 43.85; H = 2.99; Br = 26.57 per cent.

The *potassium* salt crystallises from dilute alcohol in fine, white needles:

0.4872 gave 0.1238 K<sub>2</sub>SO<sub>4</sub>. K = 11.6.

C<sub>11</sub>H<sub>8</sub>O<sub>5</sub>BrK requires K = 11.5 per cent.

A solution of the above salt in methyl alcohol, heated with methyl iodide, gave an easily saponified *ester* in the form of white needles melting at 181°:

0.1784 gave 0.1068 AgBr. Br = 25.48.

C<sub>12</sub>H<sub>11</sub>O<sub>6</sub>Br requires Br = 25.39 per cent.





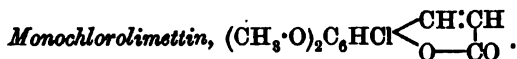
The ultimate bromination product of limettin is obtained by heating the dibromo-compound with bromine under pressure.

Five grams of dibromolimettin, 5 grams of bromine, 2 grams of iodine, and 3 c.c. of water were heated in a sealed tube at  $110^\circ$  for 3 hours. The resulting garnet-red crystals dissolved in cold alkali, but on heating the solution they decomposed. Nitrobenzene was found to be the only available solvent, and analysis showed the recrystallised substance to be still impure. On boiling these crystals, presumably consisting of the tribromodihydroxycoumarin, with acetic anhydride and allowing the solution to cool, white prisms were deposited, which crystallised from acetic acid and melted at  $244^\circ$ :

0.2432 gave 0.2812  $\text{CO}_2$  and 0.0305  $\text{H}_2\text{O}$ .  $\text{C} = 31.56$ ;  $\text{H} = 1.39$ .

0.2272 „ 0.2570  $\text{AgBr}$ .  $\text{Br} = 48.14$ .

$\text{C}_{13}\text{H}_7\text{O}_6\text{Br}_3$  requires  $\text{C} = 31.26$ ;  $\text{H} = 1.40$ ;  $\text{Br} = 48.09$  per cent.

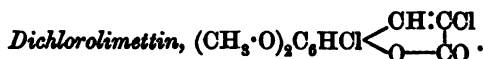


This compound is obtained when, in the preparation of trichlorolimettin, the current of chlorine is stopped as soon as the precipitate first formed has reached a maximum and re-solution begins. The precipitate crystallises from acetic acid in needles which melt at  $242^\circ$ . Long-continued boiling with 10 per cent. aqueous potash solution or with alcoholic potash has no effect on the halogen atom:

0.1462 gave 0.2934  $\text{CO}_2$  and 0.0446  $\text{H}_2\text{O}$ .  $\text{C} = 54.71$ ;  $\text{H} = 3.39$ .

0.1954 „ 0.1168  $\text{AgCl}$ .  $\text{Cl} = 14.79$ .

$\text{C}_{11}\text{H}_9\text{O}_4\text{Cl}$  requires  $\text{C} = 54.88$ ;  $\text{H} = 3.74$ ;  $\text{Cl} = 14.76$  per cent.



The final product of the action of chlorine on limettin appears to be the trichloro-derivative, whether in the presence of a "carrier" or not. The precipitate first formed when a few crystals of iodine are added has, however, very different properties from the monochloro-compound. It is much less soluble in acetic acid, and one atom of chlorine is removed from it by alkali. It melts at  $275^\circ$ :

0.1358 gave 0.2396  $\text{CO}_2$  and 0.0324  $\text{H}_2\text{O}$ .  $\text{C} = 48.12$ ;  $\text{H} = 2.65$ .

0.1546 „ 0.1592  $\text{AgCl}$ .  $\text{Cl} = 25.48$ .

$\text{C}_{11}\text{H}_8\text{O}_4\text{Cl}_2$  requires  $\text{C} = 48.0$ ;  $\text{H} = 2.9$ ;  $\text{Cl} = 25.81$  per cent.

The *monochlorocoumarilic acid*,  $(\text{CH}_3\cdot\text{O})_2\text{C}_6\text{HCl} \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}\cdot\text{CO}_2\text{H}$ , obtained from dichlorolimettin by the action of alkali, melts at  $189^\circ$ :

0.1278 gave 0.2410  $\text{CO}_2$  and 0.0434  $\text{H}_2\text{O}$ .  $\text{C} = 51.11$ ;  $\text{H} = 3.77$ .

0.1410 „ 0.0796  $\text{AgCl}$ .  $\text{Cl} = 13.96$ .

$\text{C}_{11}\text{H}_9\text{O}_5\text{Cl}$  requires  $\text{C} = 51.46$ ;  $\text{H} = 3.5$ ;  $\text{Cl} = 13.84$  per cent.

The *dichlorocoumarilic acid*,  $(\text{CH}_3\cdot\text{O})_2\text{C}_6\text{Cl}_2 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}\cdot\text{CO}_2\text{H}$ , is formed by the action of alcoholic or aqueous potash on trichlorolimettin. It melts at  $259^\circ$ :

0.2249 gave 0.3760  $\text{CO}_2$  and 0.0590  $\text{H}_2\text{O}$ .  $\text{C} = 45.59$ ;  $\text{H} = 2.91$ .

0.2244 „ 0.2188  $\text{AgCl}$ .  $\text{Cl} = 24.11$ .

$\text{C}_{11}\text{H}_8\text{O}_5\text{Cl}_2$  requires  $\text{C} = 45.36$ ;  $\text{H} = 2.74$ ;  $\text{Cl} = 24.4$  per cent.

*Disodium 4:6-dimethoxycoumarate*,  $(\text{CH}_3\cdot\text{O})_2\text{C}_6\text{H}_2 \begin{smallmatrix} \text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Na} \\ \diagup \quad \diagdown \\ \text{ONa} \end{smallmatrix}$ .

The sodium salt of dimethoxycoumaric acid separates out on heating an alcoholic solution of limettin with excess of sodium ethoxide on the water-bath. It is insoluble in absolute alcohol, but extremely soluble in alcohol containing a very small quantity of water. Washed with absolute alcohol, the salt exhibits a strongly alkaline reaction to litmus paper, owing probably to adhering ethoxide:

0.8968 gave 0.4902  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 17.60$ .

$\text{C}_{11}\text{H}_{10}\text{O}_6\text{Na}_2$  requires  $\text{Na} = 17.16$  per cent.

The silver salt is obtained by adding an excess of silver nitrate solution to the sodium salt dissolved in water. It is insoluble in water and the usual organic solvents:

0.3022 gave 0.1976  $\text{AgCl}$ .  $\text{Ag} = 49.21$ .

$\text{C}_{11}\text{H}_{10}\text{O}_6\text{Ag}_2$  requires  $\text{Ag} = 49.31$  per cent.

*4:6-Dimethoxy- $\alpha$ -methylcoumarin*,  $(\text{CH}_3\cdot\text{O})_2\text{C}_6\text{H}_2 \begin{smallmatrix} \text{CH}\cdot\text{C}\cdot\text{CH}_3 \\ \diagup \quad \diagdown \\ \text{O}-\text{CO} \end{smallmatrix}$ .

The sodium salt of limettin, when heated with absolute alcohol and methyl iodide on a water-bath, gave only regenerated limettin. The same result was also obtained by heating at  $100^\circ$  in a sealed tube, but by heating the silver salt suspended in methyl alcohol with methyl iodide for 3 hours, evaporating the alcohol off, and recrystallising the residue from acetone, white tufts of needles were deposited which melted at  $189^\circ$ . The mother liquor contained limettin. The new substance is soluble in boiling alkali, but is precipitated unchanged by acids. Analyses showed the substance to be a homologue of limettin;

0.2294 gave 0.5474 CO<sub>2</sub> and 0.1124 H<sub>2</sub>O. C = 64.98; H = 5.44.

0.1368 „ 0.3278 CO<sub>2</sub> „ 0.0664 H<sub>2</sub>O. C = 65.34; H = 5.39.

C<sub>12</sub>H<sub>12</sub>O<sub>4</sub> requires C = 65.45; H = 5.45 per cent.

*Dimethoxy-α-methyl-β-bromocoumarin*, (CH<sub>3</sub>·O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>  $\begin{matrix} \text{CBr} \cdot \text{C} \cdot \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{matrix}$ .

A solution of bromine was gradually added to homolimettin, both dissolved in acetic acid, until the colour of the bromine was permanent. The solution poured into water gave a precipitate which crystallised from acetic acid in the form of needles melting at 260°:

0.1340 gave 0.2362 CO<sub>2</sub> and 0.0422 H<sub>2</sub>O. C = 48.07; H = 3.5.

0.1882 „ 0.1172 AgBr. Br = 26.5.

C<sub>12</sub>H<sub>11</sub>O<sub>4</sub>Br requires C = 48.16; H = 3.7; Br = 26.75 per cent.

*Dimethoxy-α-methyl-β-hydroxycoumarin*, (CH<sub>3</sub>·O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>  $\begin{matrix} \text{C(OH)} \cdot \text{C} \cdot \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{matrix}$ .

The bromine atom in the monobromo-compound is readily removed by heating with alkali. The product then crystallises from dilute alcohol in minute rosettes of needles and melts at 248°. Heated with acetic anhydride, the acetyl compound formed melts at 134°. On saponification, the original substance was obtained with unaltered melting point:

0.1172 gave 0.2612 CO<sub>2</sub> and 0.0542 H<sub>2</sub>O. C = 60.78; H = 5.13.

C<sub>12</sub>H<sub>12</sub>O<sub>5</sub> requires C = 61.01; H = 5.08 per cent.

As there is no formation of a coumarilic acid when the substance is treated with alkali, the halogen in this compound must occupy the β-position relatively to the CO-group, being in this respect unlike the halogen derivatives of limettin previously described.

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## LV.—A Method of Determining the Ratio of Distribution of a Base between Two Acids.

By H. M. DAWSON and F. E. GRANT.

SEVERAL methods have been employed for determining the ratio of distribution of a base between two competing acids. These may be divided into two classes, methods belonging to the one being designated

as chemical, and those to the other as physical. Where the system under investigation is homogeneous, that is, where the substances are all in solution, the physical methods only are capable of application, and chemical analysis can furnish no information in regard to the concentrations of the reacting compounds.

Any physical changes which accompany the chemical phenomena, or physical properties which depend on the chemical arrangement of the reacting components, can be used for the determination of the equilibrium in the solution. The thermal changes accompanying the chemical transformations have been utilised by Thomsen; Ostwald has made use of the variations of the specific volume and specific refractive power, these three well known methods being of wide application and giving fairly concordant results. Jellet (*Trans. Roy. Irish. Acad.*, 25, 371) made use of optical rotatory power, and Wiedemann (*Ann. Phys. Chem.*, 1878, [iii] 5, 45) of magnetic qualities, to ascertain the equilibrium relationships, the range of applicability being in these cases, however, very small. Colorimetric and photometric measurements have also been employed, the former by Gladstone (*Phil. Mag.*, 1855, [iv], 9, 535), and by Müller (*Poggendorff's Ergänzungsband*, 1873, 6, 123), and the latter by Settegast (*Ann. Phys. Chem.*, 1879, [iii], 7, 242). The colorimetric method appears, however, only capable of yielding results of a qualitative nature.

The theory of the method used by us can be described in a few words. An aqueous solution containing two different acids and a quantity of a base insufficient for neutralisation may be regarded as containing the following components:



HA and HA' representing the two acids and MA and MA' the corresponding salts. For the sake of simplicity, the electrolytic dissociation of the reacting components is left out of account in this formulation. If this aqueous solution is shaken up with a liquid with which it is practically immiscible, and if this liquid is capable of taking up one, and one only, of the four reacting components from the aqueous solution, say the acid HA, we have at once a means of determining the concentration of each of the components in the aqueous solution if the quantities of the two acids and the base in the original solution are known. A knowledge of the ratio of distribution of HA between water and the second non-miscible liquid will enable us to calculate the concentration of the free acid HA in the aqueous solution for any given concentration in the second liquid, and since the original quantities of the two acids and the base in the aqueous solutions are known, the concentrations of the other components can be easily calculated.

As the result of preliminary experiments, it was found that when

aqueous solutions of tartaric, malic, citric, and succinic acids are shaken up with chloroform, the acid remains entirely in the water. Solutions of acetic acid, on the other hand, give up an easily measurable proportion to the chloroform layer. Each of the first mentioned acids can therefore be combined with acetic acid and the ratio of distribution of a base between these can be determined by extracting the aqueous solution with chloroform.

*Distribution of Acetic Acid between Water and Chloroform.*

From the preceding description of the method, an accurate knowledge of the ratio of distribution of acetic acid between water and chloroform is requisite. The mode of experimentation was the following. Sixty c.c. of acetic acid solution and 60 c.c. of freshly distilled chloroform were introduced into a cylindrical separating funnel, which was immersed in a thermostat maintained at 20°. At intervals of about five minutes during a period of three-quarters of an hour, the funnel was removed and the contents violently agitated. The chloroform and aqueous solution were then allowed to separate completely by leaving the funnel in the thermostat for half-an-hour, after which the two layers were run off into separate stoppered tubes. Measured portions were then titrated, the aqueous layer with  $N/4$ , and the chloroform layer with  $N/40$  sodium hydroxide, free from carbon dioxide. The results obtained are given in the following table, the concentrations being expressed in gram-equivalents per litre :

Concentration of aqueous layer. $C_1$ .	Concentration of chloroform layer. $C_2$ .	$q = \frac{C_1}{C_2}$ .
1.585	0.2277	6.74
0.9084	0.08904	10.21
0.6089	0.04557	13.37
0.3178	0.01576	20.17
0.2696	0.01222	22.07
0.2515	0.01109	22.68
0.1946	0.007586	25.66
0.1591	0.005608	28.36
0.1269	0.004061	31.23
0.09594	0.002848	33.68
0.06445	0.00174	37.04

It is evident from the numbers in the last column that the ratio of distribution of the acetic acid varies very considerably with the concentration, and that the proportion of acid in the aqueous layer increases as the absolute amount decreases. This is perhaps due to the acetic acid dissolved in the chloroform consisting largely of double

molecules, whereas in water, neglecting the small amount of electrolytic dissociation, the acid is present in the form of simple molecules. The increase of the ratio  $\frac{C_1}{C_2}$  with increasing dilution would then correspond to a gradually increasing dissociation of the double molecules in the chloroform into simple molecules.

In order to be able to determine the concentration of acetic acid in water for any given concentration in chloroform, the graphic representation in the figure has been made use of. In this diagram the concentration of the acetic acid in the chloroform  $C_2$  is represented on the abscissa, and the distribution ratio  $q$  on the ordinate. The diagram contains only the data for the smaller concentrations. Multiplication of any value of  $C_2$  by the corresponding value of  $q$  gives at once the concentration of acetic acid in the water layer.

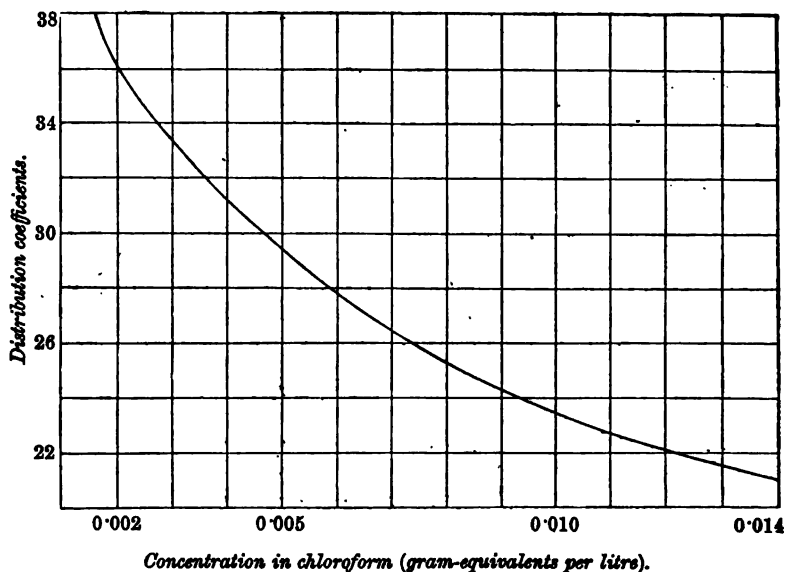
*Influence of Dissolved Acids and Salts on the Distribution of Acetic Acid between Water and Chloroform.*

In the actual experimental determination of the ratio of distribution of sodium hydroxide between acetic, and, say, tartaric acids by the method indicated above, it must be remembered that the aqueous layer contains free tartaric acid and sodium salts of the two acids. The presence of these may influence the ratio of distribution of the acetic acid between the water and the chloroform, in which case a correction would have to be made in the value of  $q$  given by the curve before the concentration of the free acetic acid in the aqueous layer could be calculated for a given concentration in the chloroform. To ascertain the order of magnitude of this influence, experiments have been made on the quantity of acetic acid extracted from aqueous solutions containing (1) sodium acetate, (2) tartaric acid. It is obviously impossible to determine experimentally the influence of sodium tartrate on the distribution of the acetic acid between the two liquids, for acetic acid would partially displace the tartaric acid from the salt. It may be assumed, however, that its influence will be approximately the same as that of sodium acetate.

The experimental data are collected in the following table, the effect of the sodium acetate or tartaric acid on the distribution of the acetic acid being clearly seen by a comparison of the values of  $q'$  with those of  $q$ , the latter being taken from the curve on p. 516. The corresponding values of  $q'$  and  $q$  are the ratios of distribution for the same concentration of acetic acid in the chloroform when the aqueous layer contains either tartaric acid or sodium acetate, or is free from these substances;

Concentration of foreign substance in aqueous solution.	Concentration of acetic acid in aqueous solution, $C_1$ .	Concentration of acetic acid in chloroform, $C_2$ .	$q' = \frac{C_1}{C_2}$ .	$q$ .
0.80 <i>N</i> sodium acetate.....	0.8012	0.01482	21.08	20.9
0.25 „ „ .....	0.2505	0.01069	23.45	23.0
0.20 „ „ .....	0.1991	0.007554	26.36	25.8
0.10 „ „ .....	0.1008	0.002938	34.31	33.8
0.25 <i>N</i> tartaric acid .....	0.2363	0.01021	23.16	23.8

The differences between the values of  $q'$  and  $q$  indicate that the sodium acetate and tartaric acid in the aqueous solution have some



influence on the ratio of distribution of acetic acid between water and chloroform. In all the experiments the influence exerted is, however very slight, and since the chief object of this paper is to describe new method of determining the distribution of a base between two acids rather than to establish more accurate values, we have assumed the influence of dissolved salts and second acid on the distribution as negligible.

*Determination of the Acetic Acid extracted by Chloroform from Aqueous Solutions containing Equivalent Quantities of Acetic Acid, Sodium Hydroxide, and a Second Acid.*

Solutions of the various acids and of sodium hydroxide of as nearly as possible normal concentrations were prepared. The acids were carefully purified, and the solution of alkali was made from metallic sodium. If equal volumes of normal solutions of sodium hydroxide, acetic acid, and, say, tartaric acid, are mixed, and the resulting solution is shaken up with chloroform, then since the latter extracts a certain amount of the acetic acid from the aqueous solution, this will no longer contain the base and the two acids in equivalent quantities. To compensate for the acetic acid thus extracted by the chloroform, this acid was added in slight excess to the original solution, so that the latter after being shaken up with chloroform would contain the acetic acid in amount equivalent to the base and the other acid present. The quantity of acetic acid thus required in excess of the other acid was determined approximately by consideration of the curve.

The exact method of experimentation and calculation will be seen best if one of the determinations is considered in detail.

Twenty c.c. of *N*-tartaric acid, 20 c.c. of *N*-sodium hydroxide, and 20.7 c.c. of *N*-acetic acid were introduced into a graduated flask and the mixture diluted to 100 c.c.; 60 c.c. of this solution were then shaken up as previously described with 60 c.c. of chloroform. Titration of the aqueous layer gave 0.1990, that of the chloroform 0.005632 gram equivalents per litre. From the first titration number, we may write down the concentrations of the acids and base in the aqueous solution. In gram-equivalents per litre they are 0.200 of tartaric acid, 0.200 of sodium hydroxide, and 0.199 of acetic acid. From the curve, the distribution ratio of acetic acid between water and chloroform at a concentration in the latter solvent of 0.005632 gram equivalents per litre is found to be 28.3. The product,  $28.3 \times 0.005632 = 0.1593$ , gave the concentration of the free acetic acid in the aqueous layer. The acetic acid present as sodium acetate is  $(0.199 - 0.1593) = 0.0397$  gram-equivalents per litre, and this number represents also the concentration of the free tartaric acid. Finally, the tartaric acid in combination with the base is  $(0.200 - 0.0397) = 0.1603$  gram-equivalents per litre. The ratio of the amount of tartaric to that of acetic acid in combination with the base is therefore  $\frac{0.1603}{0.0397} = 4.04$ .

Similar experiments on the distribution of sodium hydroxide between acetic and tartaric acids to that just described have been carried out at other concentrations. In the strongest solution, the concentration



of each of the two acids and the base was 0.3 *N*, in the next 0.25 *N*, in the third, 0.2 *N*, and in the most dilute solution, 0.1 *N*.

The same concentrations were employed in corresponding series of experiments, in which the tartaric acid was replaced successively by citric, malic, and succinic acids. The tables on p. 519 contain the data calculated from the experiments. The first column gives the concentrations of the two acids and the base in the aqueous solution after shaking up with chloroform; the second gives the concentration of the acetic acid in the chloroform layer; the third, the corresponding value of the distribution coefficient *q*. In the fourth, the concentrations of the free acids in the aqueous solutions are given, the fifth containing that of the combined acids, all concentrations being expressed in gram-equivalents per litre. The last column contains the ratio of the amount of combined tartaric (citric, malic, succinic) acid to that of the combined acetic acid.

The accuracy attainable in the determination of the ratio given in the last column is smaller the smaller the concentration, the amount of acetic acid in the chloroform layer decreasing rapidly with the concentration of the solutions and becoming very small when the acids and base are present in 0.1 *N*-concentration. For this reason, experiments with 0.1 *N*-solution were not carried out in the case of malic and succinic acids.

An assumption, not yet mentioned, has been made in connection with the calculation of the above results, namely, that no sensible change of volume takes place in the aqueous solution when the latter is shaken up with an equal volume of chloroform. Herz (*Ber.*, 1898, 31, 2669) found that, at 22°, 100 volumes of water dissolve 0.42 volume of chloroform, whilst 100 volumes of the latter are capable of taking up 0.152 volume of water. We may conclude that the aqueous solution on being shaken up with chloroform undergoes a slight alteration of volume. To ascertain the order of magnitude of this alteration under our conditions of experimentation, 0.25 *N*-citric acid solution was shaken up at 20°, with an equal volume of chloroform and the concentration of the acid in the aqueous solution compared with that in the original solution. The concentrations were:

Original solution.....	0.2519	gram-equivalents per litre.
After shaking with chloroform	0.2508	" " "

The volume of the aqueous solution then undergoes a slight increase after shaking with the chloroform, but for the reason previously stated this small alteration has not been taken into account in the above calculations.

Although an attempt was made to obtain solutions containing the acids and base in exactly equivalent quantities, inspection of the

Composition of aqueous solution.	Concentration of acetic acid in chloroform.	g.	Concentration of free acids in aqueous solution.	Concentration of combined acids in aqueous solution.	Ratio of quantities of combined acids.
{ 0.800 tartaric 0.800 NaOH 0.3031 acetic 0.250 tartaric 0.250 NaOH 0.2502 acetic 0.200 tartaric 0.200 NaOH 0.199 acetic 0.100 tartaric 0.100 NaOH 0.1017 acetic	0.0108  0.00822  0.005632  0.00224	22.9  25.0  28.3  34.9	{ Tartaric 0.0558 Acetic 0.2473 { Tartaric 0.0447 Acetic 0.2055 { Tartaric 0.0397 Acetic 0.1593 { Tartaric 0.0235 Acetic 0.0782	Tartaric 0.2441 Acetic 0.0558 Tartaric 0.2053 Acetic 0.0447 Tartaric 0.1608 Acetic 0.0397 Tartaric 0.0765 Acetic 0.0235	4.38  4.59  4.04  3.26

*Acetic and Citric Acids.*

{ 0.8015 citric 0.800 NaOH 0.3049 acetic 0.2512 citric 0.250 NaOH 0.2522 acetic 0.201 citric 0.200 NaOH 0.1983 acetic 0.1005 citric 0.100 NaOH 0.1004 acetic	0.00700  0.005185  0.008682  0.001516	26.4  29.1  32.0  37.9	{ Citric 0.1216 Acetic 0.1848 { Citric 0.1040 Acetic 0.1494 { Citric 0.0815 Acetic 0.1178 { Citric 0.0485 Acetic 0.0574	Citric 0.1799 Acetic 0.1201 Citric 0.1472 Acetic 0.1023 Citric 0.1195 Acetic 0.0805 Citric 0.0570 Acetic 0.0430	1.50  1.43  1.48  1.33
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*Acetic and Malic Acids.*

{ 0.800 malic 0.800 NaOH 0.2998 acetic 0.250 malic 0.250 NaOH 0.250 acetic 0.200 malic 0.200 NaOH 0.1999 acetic	0.008204  0.006046  0.004386	25.0  27.7  30.5	{ Malic 0.0942 Acetic 0.2051 { Malic 0.0825 Acetic 0.1675 { Malic 0.0662 Acetic 0.1337	Malic 0.2058 Acetic 0.0942 Malic 0.1675 Acetic 0.0825 Malic 0.1338 Acetic 0.0662	2.08  2.08  2.02
---	--	------------------------------	---	---	------------------------------

*Acetic and Succinic Acids.*

{ 0.8006 succinic 0.800 NaOH 0.3027 acetic 0.800 succinic 0.800 NaOH 0.3034 acetic 0.2505 succinic 0.250 NaOH 0.2535 acetic 0.2004 succinic 0.200 NaOH 0.1986 acetic	0.005594  0.005781  0.004352  0.003078	28.4  28.1  30.5  33.4	{ Succinic 0.1444 Acetic 0.1589 { Succinic 0.1410 Acetic 0.1624 { Succinic 0.1213 Acetic 0.1327 { Succinic 0.0964 Acetic 0.1026	Succinic 0.1562 Acetic 0.1438 Succinic 0.159 Acetic 0.141 Succinic 0.1292 Acetic 0.1209 Succinic 0.1040 Acetic 0.0960	1.09  1.13  1.07  1.08
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numbers in the first column will show that this is only approximately the case. The greatest deviations are found in the first and third experiments with citric acid. It is possible by applying the law of mass action to the equilibrium in the solution to correct for these deviations from exact equivalency. This has been done in the case of the experiments mentioned, but the corrected values (1.51 and 1.47) differ to an inappreciable extent from the numbers (1.50 and 1.48) actually obtained. The differences are well within the errors of experiment and the numbers given in the last column may accordingly be taken to represent the ratios of the combined acids when these are present in equivalent quantities.

It may be of interest to compare the above numbers with the values of the ratio of distribution obtained by other static methods. The results obtained by the thermochemical method are scarcely accurate enough to admit of a rigorous comparison. Ostwald's measurements of volume and specific refractive power were made at approximately  $N/3$  concentration, and those on the solution of calcium oxalate by different acids at  $N$  and  $N/10$  concentrations. The following table contains the data which may be regarded as comparable, the older numbers having been recalculated so as to make acetic acid the basis of comparison :

	New method. Concentration 0.3 <i>N</i> .	Volume method (Ostwald). Concentration 0.33 <i>N</i> .	New method. Concentration 0.1 <i>N</i> .	Calcium oxalate method (Ostwald). Concentration 0.1 <i>N</i> .
Tartaric .....	4.38	4.23	3.26	1.93
Malic .....	2.08	2.30	—	1.64
Citric .....	1.50	—	1.33	1.96
Succinic .....	1.11	1.18	—	1.27
Acetic .....	1.00	1.00	1.00	1.00

The first two series of numbers agree very well, but at the smaller concentration considerable deviations are found. This is to be expected since the two series of values given by Ostwald can scarcely be reconciled with each other. Such large changes in the relative values are scarcely probable for such a small change of concentration.

Finally, it may be pointed out that the above method of experimentation will serve equally well to determine the ratio of distribution of an acid between two bases. The necessary condition is that some liquid, not miscible to any extent with water, can be found, which will extract in conveniently measurable quantity one of the four reacting components. It can be shown that even if two of the components, say the two acids, are extracted by the second liquid, yet under

certain conditions the ratio of distribution of the base in the aqueous solution can be measured.

Suppose that of the components  $HA$ ,  $MA$ ,  $MA'$  and  $HA'$ , present in the aqueous solution,  $HA$  and  $HA'$  are taken up by the second liquid. Let  $q$  be the ratio of distribution of  $HA$ , and  $q'$  that of  $HA'$  between water and the second liquid. Suppose in any experiment, the total concentration of acid in the second liquid  $= C_1$ , then  $C_1 = C_{HA} + C_{HA'}$ , and the concentration of free acid in the water  $= C_2$ , then  $C_2 = qC_{HA} + q'C_{HA'}$ . From the values  $C_1$  and  $C_2$ , determined experimentally, it will obviously be possible to calculate the concentrations of each of the two acids in the second liquid, and therefore the concentrations of the free acids  $qC_{HA}$  and  $q'C_{HA'}$  in the aqueous solution, provided the values of the distribution ratio  $q$  and  $q'$  are sufficiently different from each other. In the case where  $q = q'$ , then the individual concentrations of the two acids cannot be determined at all. It is supposed, in this description of the method, that the presence of the dissolved salts and second acid in the water, and that of the second acid in the chloroform, has no effect on the distribution of the first acid and *vice versa*.

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## LVI.—*The Molecular Complexity of Acetic Acid in Chloroform Solution.*

By H. M. DAWSON.

THE experimental results communicated in the previous paper show that the ratio of distribution of acetic acid between water and chloroform increases very considerably with increase of the dilution. It has been there suggested that this is due to the gradual splitting up of the double acetic acid molecules, which are supposed to be present in solvents not containing the hydroxyl group, into simple molecules. With the object of testing this assumption, the equation of the dissociation isotherm has been applied to the acetic acid dissolved in the chloroform, the experimental data in the previous paper being utilised for the purpose of calculation. As will appear from what follows, the concentrations of acetic acid in chloroform which have been used correspond to a region of almost complete molecular transformation.

As before, let  $c_1$  and  $c_2$  represent corresponding concentrations of acetic acid in water and in chloroform. If  $\alpha$  is the degree of dissociation of the acid in the aqueous solution at this concentration, then  $c_1(1 - \alpha)$

is the concentration of the undissociated molecules. If  $r$  is the ratio of distribution of the simple molecules between water and chloroform,  $\frac{c_1(1-a)}{r}$  will be the concentration of the simple acetic acid molecules in the chloroform, and  $c_2 - \frac{c_1(1-a)}{r}$  that of the associated molecules.

Applying the law of mass action, the result obtained is:

$$\frac{\left\{ \frac{c_1(1-a)}{r} \right\}^2}{c_2 - \frac{c_1(1-a)}{r}} \quad \text{or} \quad \frac{c_1^2(1-a)^2}{r^2 c_2 - r c_1(1-a)} = K,$$

where  $K$  is a constant.

By taking the second and the seventh experiments (see first table in previous paper) as a basis, and assuming that the experimental data for these give the same value for  $K$ , the value of  $r$  is calculated to be 42.9.

For each of the eleven experiments on the distribution of acetic acid the value of the above expression for the constant  $K$  has been calculated by inserting the experimental numbers for  $c_1$  and  $c_2$ , the value for  $r = 42.9$ , and that for  $a$  obtained from Ostwald's dilution formula which, in the case of acetic acid at  $25^\circ$ , is  $\frac{\alpha c}{1-a} = 0.000018$ .

The following table contains these values of  $K$  as well as the concentrations of the simple and double acetic acid molecules in the chloroform, these concentrations being expressed in gram-equivalents per litre:

Concentration of undissociated acetic acid in water.	Concentration of simple molecules in $\text{CHCl}_3$ .	Concentration of double molecules in $\text{CHCl}_3$ .	$K$ .
1.530	0.03565	0.1920	0.0066
0.9048	0.02109	0.06795	0.0065
0.6052	0.01411	0.03146	0.0063
0.3156	0.007355	0.008405	0.0064
0.2675	0.006234	0.005986	0.0065
0.2496	0.005816	0.005274	0.0064
0.1929	0.004495	0.003091	0.0065
0.1574	0.003669	0.001939	0.0069
0.1254	0.002922	0.001139	0.0075
0.09469	0.002207	0.000641	0.0076
0.06386	0.001477	0.000263	0.0083

The constancy of the values of  $K$  in the last column leads to the conclusion that the assumption of a gradual dissociation of the double acetic acid molecules in the chloroform into simple molecules with increasing

dilution is correct. The maximum and minimum values of  $K$  for the first eight experiments are 0.0069 and 0.0063 respectively. The limiting concentrations of acetic acid in the chloroform which give this constant value of  $K$  are 0.23 and 0.006 gram-equivalents per litre, the ratio of these concentrations being approximately 40 to 1. For the most dilute solutions which have been investigated, the deviations of  $K$  from the mean value are more considerable and increase with the dilution. At these very small concentrations, however, it must be remembered that the denominator in the first expression given above for  $K$ , representing as it does the concentration of the double acetic acid molecules, is the small difference between two gradually decreasing and approximating quantities, and a small error in the estimation of the amount of acetic acid in the water and chloroform layers would explain this gradually increasing value of  $K$ . To show that this is the case, we may, for the experimental data at the smallest concentration investigated, assume the true value of  $K$  to be the mean of the values found at the higher concentrations, namely, 0.0065, and calculate inversely the concentration of the acetic acid in the chloroform layer. We have then in the expression :

$$\frac{c_1^2(1-a)^2}{r^2c_2 - rc_1(1-a)} = 0.0065,$$

$c_1 = 0.06445$ ,  $a = 0.017$ ,  $r = 42.9$ , from which the value of  $c_2$ , the concentration of the acetic acid in the chloroform, is calculated to be 0.00181, whereas the number found by experiment is 0.00174. The difference is less than 4 per cent., and since in this experiment less than 4 c.c. of  $N/40$  sodium hydroxide were required for the titration of 50 c.c. of the chloroform solution, it is obvious that an error of about 0.15 c.c. in the titration would completely account for the discrepancy between the numbers.

It is of interest to note the considerable difference in the relative proportions of the simple and double acetic acid molecules within the limits of concentration investigated. At the highest concentration, the acetic acid present in the form of double molecules is more than five times as large as that present in the form of simple molecules, whilst at the lowest concentration the proportion is less than one-fifth. The value 42.9 calculated for the ratio of distribution of the simple acetic acid molecules between water and chloroform at 20°, when compared with the highest ratio of distribution determined experimentally, 37.04, would indicate that at concentrations only slightly less than the smallest actually investigated, the acetic acid in the chloroform would consist practically completely of simple molecules. It was not considered advisable to carry out experiments at higher concentrations, for the addition of acetic acid to a mixture of chloro-

form and water increases the mutual solubility of these liquids, and this increase is only terminated by complete miscibility.

A similar dissociation of the double molecules of acetic acid into simple ones has been observed in benzene solutions (Nernst, *Zeit. physikal. Chem.*, 1891, 8, 110; Hendrixson, *Zeit. anorg. Chem.*, 1897, 13, 73). Such results are interesting from the fact that it is generally assumed that substances containing the hydroxyl group, when dissolved in liquids which do not contain this group, are polymerised. It would appear, however, that such a polymerisation is essentially dependent on the concentration, and that if the latter is sufficiently decreased these substances containing the hydroxyl group will assume the simplest molecular condition. Further interest is attached to the results in view of the recently expressed opinion (Walden and Centnerszwer, *Zeit. physikal. Chem.*, 1902, 39, 513) that substances entering into solution have quite generally the tendency to form polymerised molecules or complex associated molecules in which one or more molecules of the solvent are contained.

It may be noted, finally, that the distribution method is particularly well suited for the investigation of molecular dissociation phenomena, which only take place at high degrees of dilution. The freezing point and boiling point methods, which are convenient for more concentrated solutions, are in such cases quite useless.

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## LVII.—*The Existence of Polyiodides in Nitrobenzene Solution. I.*

By H. M. DAWSON and R. GAWLER.

IN the course of some experiments on the ratio of distribution of iodine between nitrobenzene and a solution of potassium iodide, one of us obtained some apparently very peculiar results, and the inquiry into the cause of these abnormalities has furnished the material contained in the following paper.

The nature of the observations which served as the starting point of our investigation may be stated very briefly. A series of experiments was carried out in which a mixture of 20 c.c. of nitrobenzene and 30 c.c. of *N*/10 potassium iodide solution was shaken up with gradually increasing quantities of iodine, and the amount of iodine in each layer determined by titration with sodium thiosulphate. The numbers obtained are given below, the concentrations being expressed in grams per litre:

Aqueous solution.	Nitrobenzene.	Aqueous solution.	Nitrobenzene.
0.3890 gram	14.79 grams	1.161 grams	82.83 grams
0.7117 "	30.89 "	1.157 "	140.4 "
0.9872 "	49.0 "	0.7731 "	168.5 "
1.073 "	56.63 "	0.7567 "	187.4 "

It will be observed that as the amount of iodine added to the mixture increases, the iodine concentration in the aqueous solution at first increases, passes through a maximum, and then decreases. The only possible explanation of this peculiar phenomenon seemed to be that the nitrobenzene extracts the potassium iodide from the aqueous solution, thereby diminishing the solvent power of the latter for iodine. Distillation of some of the nitrobenzene solution at once proved the correctness of this assumption, for a considerable quantity of potassium iodide was left behind.

Experiments were then carried out to ascertain how the quantity of potassium iodide thus taken up from a given volume of the aqueous solution by the nitrobenzene depends on the volume of the latter and on the quantity of iodine added. In the first series, the volume of the nitrobenzene was constant, namely, 20 c.c., this being shaken up at constant temperature (20°) with 50 c.c. of *N*/10 potassium iodide solution after addition of an accurately weighed quantity of iodine. After the attainment of equilibrium, a measured portion of the aqueous solution was evaporated, and in this manner the quantity of potassium iodide remaining in the latter was determined. The numbers obtained are collected in the following table:

Iodine added.	Potassium iodide in aqueous solution.	Potassium iodide in nitrobenzene.
—	0.8317 gram	—
1.00 grams	0.5584 "	0.2716 gram
1.50 "	0.4497 "	0.3803 "
2.00 "	0.3561 "	0.4739 "
2.50 "	0.2729 "	0.5571 "
3.00 "	0.2064 "	0.6236 "
3.50 "	0.1549 "	0.6751 "
(5.00) "	0.0680 "	0.7620 "

In the last experiment, the iodine added to the system was not completely brought into solution, although the liquids were shaken for a very considerable time. The numbers given for the potassium iodide in the nitrobenzene are obtained by subtraction (50 c.c. of *N*/10 potassium iodide solution containing 0.83 gram of potassium iodide).

From the above table, it is clear that addition of iodine results in the transference of potassium iodide from the aqueous solution



to the nitrobenzene. As the amount of iodine increases, the quantity of potassium iodide extracted from the aqueous solution also increases, although less rapidly, as is seen by the fact that the first gram of iodine causes the removal of 0.27 gram, the second of 0.20, and the third only of 0.15 gram of potassium iodide. The last experiment shows further that almost the whole of the iodide in the aqueous solution can thus be removed by the nitrobenzene if a sufficient quantity of iodine is added.

In a second series of experiments, the same quantity, namely, 2 grams, of iodine was added to the 50 c.c. of  $N/10$  potassium iodide solution (containing 0.83 gram of potassium iodide), whilst the volume of the nitrobenzene was varied; the numbers are tabulated below:

Volume of nitrobenzene in c.c.	20.	30.	40.	50.
Gram of potassium iodide in 50 c.c. aqueous solution after shaking with nitrobenzene...	0.3561	0.3346	0.3220	0.3130

The numbers indicate that the amount of potassium iodide extracted from the aqueous solution by the addition of a fixed quantity of iodine increases with the volume of nitrobenzene employed. This increase is, however, relatively small, and it is evident that the most important factor in the determination of the amount of potassium iodide extracted from the aqueous solution is the quantity of added iodine. We may now give the results of a third series of experiments similar to those already described, in which, however, the distribution of the iodine, as well as that of the potassium iodide between the two liquids, was determined. Approximately weighed quantities of iodine were added to a mixture of 20 c.c. of nitrobenzene and 50 c.c. of  $N/5$  potassium iodide solution. After shaking thoroughly at  $20^\circ$ , the concentration of the potassium iodide in the aqueous solution was determined by evaporation, and that of the iodine in both layers by titration with sodium thiosulphate. The iodine in the nitrobenzene could be determined quite accurately by means of sodium thiosulphate solution and starch paste if well shaken up in a stoppered bottle. The numbers contained in the table on p. 527 represent the concentrations in gram-molecules per litre.

The concentration of the potassium iodide in the nitrobenzene was determined by difference, neglecting the changes of volume which take place in the two solvents; in the case of the more highly concentrated solutions, these may, however, attain a considerable magnitude, and the numbers in the third column are certainly too low. The table shows clearly that the apparently abnormal variation of the iodine concentration in the aqueous solution which is seen in the numbers in the third column is due to the removal of the

Iodine added in grams.	Concen- tration KI in aqueous solution.	Concen- tration I <sub>2</sub> in aqueous solution.	Concen- tration KI in nitrobenzene.	Concen- tration I <sub>2</sub> in nitrobenzene.	Ratio $\frac{I_2}{KI}$ in nitrobenzene.
1.08	0.1618	0.005183	0.09548	0.1866	1.954
1.71	0.1408	0.007468	0.1494	0.3045	2.088
1.91	0.1347	0.008474	0.1632	0.3394	2.079
2.5	0.1192	0.01	0.2019	0.4411	2.185
3.08	0.1087	0.01117	0.2407	0.5461	2.268
5.02	0.0618	0.01236	0.3455	0.8387	2.428
7.03	0.03237	0.01084	0.4178	1.154	2.764

potassium iodide from the aqueous solution by the nitrobenzene, whereby the solvent power of the former for iodine is diminished and that of the latter increased. The experimental observations which formed the basis of the investigation are therefore in all probability explained by the great solvent power of nitrobenzene for certain polyiodides which are formed, this solvent power being even greater than that of water.

It is perhaps possible to subject the above experimental results to a more minute analysis. By means of the equation which determines the equilibrium between the iodide, tri-iodide, and free iodine in the aqueous solution (Jakowkin, *Zeit. physikal. Chem.*, 1894, 13, 539 ; 1896, 20, 19 ; Dawson, *Trans.*, 1901, 79, 238), the concentration of the free iodine in the aqueous solution can be calculated from the potassium iodide, and total iodine concentrations determined experimentally. Multiplication of this by the value of the ratio of distribution of iodine between nitrobenzene and water, which in two experiments at concentrations of 18 and 35 grams of iodine per litre of nitrobenzene was found to be 186.4 and 187.2 respectively, gives us the concentration of the free iodine present in the nitrobenzene. That portion of iodine in the nitrobenzene which is in chemical combination with the potassium iodide can thus be determined. On account of the complicated nature of the relationships, we have, however, refrained from speculations based on these calculations.

Since the distribution experiments do not give in a simple manner any definite information in regard to the existence of any particular polyiodides in the nitrobenzene solution, we have attempted to ascertain the nature of these by solubility determinations. Whilst potassium iodide is practically insoluble in nitrobenzene, a preliminary experiment showed that if the nitrobenzene contains iodine it readily dissolves a considerable quantity of potassium iodide. Before such solubility determinations could be carried out, it was necessary to have a method of analysing the solutions of iodine and potassium iodide in nitrobenzene. The iodine

is readily determined with sodium thiosulphate by shaking in a stoppered bottle. Several methods were tried for the estimation of the potassium iodide before a sufficiently accurate and trustworthy process was discovered. The method finally adopted consists in distilling a measured volume of the nitrobenzene solution in steam. Ten c.c. or less of the dark brown solution are introduced into a hard glass flask, a little water added, and a current of steam passed through the mixture, when the iodine and nitrobenzene distil over. In about twenty minutes, the whole of the iodine and practically all the nitrobenzene have passed over and an aqueous solution of potassium iodide is left in the flask, the solution being usually slightly yellow in colour owing to a little nitrobenzene which remains dissolved. This aqueous solution, after cooling, is extracted four or five times with carefully purified carbon disulphide to remove the nitrobenzene, evaporated to dryness in a platinum basin on the water-bath, and the residue gently heated over a free flame. The residue obtained in this manner is perfectly white and consists of the potassium iodide contained in the nitrobenzene solution subjected to distillation. Blank experiments with known quantities of potassium iodide and variable quantities of iodine and nitrobenzene showed that this method of analysis is capable of yielding good results.

*Solubility of Iodine and Potassium Iodide in Nitrobenzene.*

The solubility determinations were made in a stoppered bottle attached to the circumference of a rotating wheel driven by a small hot-air engine. The temperature was that of the room, and was therefore not very constant; but for the object of the investigation this was of no consequence. The time of rotation ranged from ten to thirty hours. As previously stated, potassium iodide is insoluble in nitrobenzene, whilst two determinations of the solubility of iodine gave 50.71 and 50.53 grams per litre at 16—17°. The mean of these is 50.62, or 0.200 gram-molecule per litre. The experiments in which solutions were obtained containing both iodine and potassium iodide can be divided into two series. In the first series, the solubility of potassium iodide in nitrobenzene containing different quantities of iodine was investigated, the resulting solutions being saturated with regard to potassium iodide, but not so with reference to iodine. The experiments in the second series relate to the solubility of iodine in nitrobenzene containing potassium iodide, these solutions being saturated only with regard to iodine. Tables I and II contain the solubility numbers, the concentrations being expressed in grams and gram-molecules per litre:

I. *Solubility of Potassium Iodide in Nitrobenzene containing Iodine.*

Concentration of iodine.		Concentration of potassium iodide.		Ratio $\frac{I_2 \text{ mols.}}{KI \text{ mols.}}$
Grams per litre.	Gram-mols. per litre.	Grams per litre.	Gram-mols. per litre.	
18.02	0.0710	12.31	0.0741	0.985
29.97	0.1181	19.71	0.1186	0.994
38.83	0.1531	25.13	0.1514	1.01
58.25	0.2296	38.70	0.2331	0.985
71.61	0.2823	45.41	0.2736	1.03
144.2	0.5684	81.98	0.4939	1.15
144.3	0.569	80.38	0.484	1.18
210.8	0.881	111.4	0.671	1.24
411.2	1.621	164.0	0.988	1.64
597.8	2.357	211.9	1.276	1.85
658.8	2.596	221.0	1.331	1.95
695.8	2.743	235.7	1.420	1.93

It is interesting to note what relatively large quantities of iodine and potassium iodide can be dissolved in nitrobenzene when both of these substances are present together. Although potassium iodide itself is insoluble, and iodine only dissolves to the extent of 50 grams per litre, yet the most concentrated of the above solutions contains about 240 grams of potassium iodide and 700 grams of iodine. The action of chemical affinities, resulting in the formation of polyiodides, is obviously the cause of these remarkable solubility phenomena. The last column in the table furnishes us with a means of ascertaining the nature of the complex compounds. In the first five experiments, the molecular ratio of iodine to potassium iodide is constant and equal to unity; in other words, at low concentrations one molecule of potassium iodide dissolves in the nitrobenzene for each molecule of iodine present. The conclusion to be drawn from this is that the triiodide,  $KI_3$ , is formed. The amount of potassium iodide which dissolves when the nitrobenzene contains more than about 0.3 gram-mol. of iodine per litre is, however, less than the molecular equivalent, and with increasing iodine concentration the molecular ratio of iodine to potassium iodide continually increases, attaining a value nearly twice as great as that which it has in the dilute solutions. There is here undoubted evidence of the formation of a higher polyiodide (or polyiodides), but its composition is not determinable from the available data.

The data in the table on p. 530 refer to solutions saturated with regard to iodine, but not, to potassium iodide. Under these circumstances, it will be observed that a solution can be obtained containing

II. *Solubility of Iodine in Nitrobenzene containing Potassium Iodide.*

Concentration of iodine.		Concentration of potassium iodide.		Ratio $\frac{I_2 \text{ mola.}}{K \text{ mola.}}$
Grams per litre.	Gram-mols. per litre.	Grams per litre.	Gram-mols. per litre.	
112.7	0.4439	12.35	0.0744	5.97 (3.28)
179.3	0.7065	24.35	0.1467	4.82 (3.45)
295.7	1.166	45.56	0.2745	4.25 (3.52)
404.7	1.595	65.56	0.395	4.04
511.7	2.017	82.60	0.4976	4.05
698.2	2.752	115.8	0.698	3.94
851.0	3.355	143.1	0.862	3.89
941.3	3.713	156.6	0.943	3.94
943.6	3.719	155.2	0.935	3.98

approximately 950 grams of iodine and 160 grams of potassium iodide per litre. On comparing one of these solutions with one of those in the first solubility table containing approximately the same quantity of iodine, it is found that the corresponding quantities of potassium iodide are very different. For this purpose, we may take the solutions containing 700 grams of iodine per litre. When this solution is saturated with reference to potassium iodide, it contains 236 grams of the latter per litre; but when it contains 700 grams of iodine, and is saturated with regard to this substance, then it contains only 116 grams of potassium iodide. The last column in the table shows that the molecular ratio of iodine to potassium iodide at first decreases rapidly with increasing concentration, and then becomes practically constant. Within the errors of experiment, the value of this molecular ratio for the last six solubility determinations is equal to four. It must be pointed out that the theoretical treatment of the solubility data in this case where the solutions are saturated with regard to iodine, is not so simple as in the case where they are saturated with reference to potassium iodide. The reason of this is to be found in the fact that, whereas potassium iodide is practically insoluble in nitrobenzene, iodine at the ordinary temperature dissolves to the extent of 0.2 gram-mol. per litre. Before it is possible, therefore, to draw conclusions with regard to the nature of the chemical complexes, the formation of which is the cause of the greatly increased solubility of the iodine, we must take account of the quantity of iodine which is present in the nitrobenzene solution in the free and uncombined condition. To do this quantitatively is a matter of some difficulty. It may safely be said that the free iodine concentration

which corresponds to the condition of saturation with regard to solid iodine, will diminish as the solution becomes more concentrated with respect to the other components of the solution, namely, the polyiodides, and in the most concentrated solutions represented in the previous table is probably much smaller than in pure nitrobenzene. A continually decreasing quantity must therefore be subtracted from the total iodine concentration as the solution increases in concentration, in order to obtain the quantity of iodine which has entered into chemical combination with the potassium iodide. With the data at disposal, it is, however, impossible to determine the quantity of iodine which must in this manner be subtracted. The numbers in brackets in the last column are the values of the molecular ratio of iodine to potassium iodide obtained by subtracting from the total iodine concentration the quantity representing the solubility of iodine in pure nitrobenzene. These numbers are all less than four, and gradually increase with increasing concentration of the solution, whilst those representing the ratio of the total iodine to potassium iodide are greater than four and gradually decrease. It is therefore possible that a knowledge of the true values of the free iodine concentration in the various solutions would lead to values of the molecular ratio of combined iodine to potassium iodide for the dilute solutions approximately equal to four. Assuming that this is the true ratio of the chemically combined halogen and potassium iodide, the concentration of the free iodine in the various solutions can be calculated from the experimental data. In the first, second, and third solutions, these concentrations are respectively 0.146, 0.120, and 0.068 gram-mol. per litre, whereas in pure nitrobenzene the concentration of the saturated solution of iodine is 0.20 gram-molecule per litre. The sequence of these numbers is obviously that which could be theoretically anticipated, and their order of magnitude indicates that the correction which would have to be introduced for the presence of the free iodine in the more concentrated solutions becomes almost negligible. The conclusions to be drawn from the relationships exhibited by the solubility data contained in the previous table must therefore be based on the following results. In all the concentrated solutions the ratio of iodine to potassium iodide is equal to four. Taking account of the concentration of the free iodine present in the solution, this is probably the value of the molecular ratio of combined iodine to potassium iodide in the dilute solutions. The correction factor for the free iodine becomes very small in the case of the concentrated solutions, and therefore the value of the ratio of total iodine to potassium iodide is at once a measure of the ratio of combined iodine to potassium iodide. Four molecules of iodine are thus found to be chemically combined with one molecule of

potassium iodide, and we conclude that the nitrobenzene solution contains the polyiodide  $KI_3$ .

The very concentrated solutions of iodine and potassium iodide in nitrobenzene which have been obtained by us are viscous, dark-brown, almost black, liquids. Attempts to isolate the polyiodides by cooling down the concentrated solutions in a mixture of ice and salt, and by the addition of other liquids, such as benzene, carbon disulphide, and carbon tetrachloride, have not been successful. Apparently, the only effect of the addition of these liquids is to precipitate potassium iodide from the solution. It has been observed that the most concentrated solutions are very deliquescent, this property being probably characteristic of the polyiodides existing in the solution. The crystals of potassium triiodide obtained by Johnson (*Trans.*, 1877, 31, 249) were found to be extremely deliquescent. In some cases, the specific gravities of the solutions were determined. The knowledge of the specific gravity, combined with that of the concentration of the iodine and potassium iodide in the nitrobenzene solution, completely determines the relative proportions of the three components. These measurements were made with the view of ascertaining whether any simple molecular ratio exists between the nitrobenzene and the other components in the concentrated solutions; but the function of the nitrobenzene is, apparently, simply that of a solvent, for the numbers indicate no simple molecular relationship. The most concentrated solution examined had a sp. gr. 2.00.

#### *Electrical Conductivity of Nitrobenzene Solutions containing Iodine and Potassium Iodide.*

From the high value of the dielectric constant of nitrobenzene, namely, 36.2 (Turner, *Zeit. physikal. Chem.*, 1900, 35, 403), it might be expected that this solvent would have a considerable electrolytic dissociating power. This should be the case, at any rate, if nitrobenzene does not form an exception to the Nernst-Thomson rule. The only experiments which have been made in this direction are those of Kahlenberg and Lincoln, who investigated the electrical conductivity of nitrobenzene solutions containing ferric chloride, stannous chloride, bismuth chloride, and antimony trichloride. These solutions were found to have a comparatively small conducting power (*J. Physical Chem.*, 1899, 3, 12).

We have investigated the conductivity of nitrobenzene solutions containing iodine and potassium iodide, and find that the solutions are remarkably good conductors of electricity. The method employed was that of Kohlrausch, in which an ordinary Arrhenius conductivity vessel was used, the resistance capacity of which was 0.1424, and the temperature 18°. Two solutions were prepared each containing approximately

25 grams of potassium iodide per litre, one of them being saturated with reference to iodine, the other with reference to potassium iodide. When the solutions had become saturated, the solid matter was allowed to settle, and 20 c.c. of the solution were introduced into the conductivity vessel. The influence of dilution on the conductivity was determined in each case by the successive removal of 10 c.c. of the solution and addition of 10 c.c. of nitrobenzene. The experimental results are given below, the first column giving the concentration of potassium iodide in gram-molecules per litre ( $c$ ), the second the specific conductivity ( $K$ ), and the third, the molecular conductivity ( $\frac{1000K}{c}$ ), the conductivities being expressed in terms of the new unit (Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*).

*Solution saturated with regard to Iodine.*

Composition of original solution : 24.60 grams = 0.1482 gram-mol. potassium iodide per litre ; 175.7 grams = 0.6926 gram-mol. iodine per litre.

Molecular concentration of potassium iodide. ( $c$ ).	Specific conductivity. ( $K$ ).	Molecular conductivity. $\frac{1000K}{c}$ .
0.1482	0.002814	18.99
0.0741	0.001552	20.94
0.03705	0.0008476	22.88
0.01852	0.000455	24.57

*Solution saturated with regard to Potassium Iodide.*

Composition of original solution : 25.00 grams = 0.1506 gram-mol. potassium iodide per litre ; 38.39 grams = 0.1513 gram-mol. iodine per litre.

Molecular concentration of potassium iodide. ( $c$ ).	Specific conductivity. ( $K$ ).	Molecular conductivity. $\left(\frac{1000K}{c}\right)$ .
0.1506	0.003151	20.92
0.0753	0.001754	23.29
0.03765	0.0009276	24.68
0.01882	0.0005014	26.63
0.00941	0.0002662	28.29
0.00470	0.0001398	29.61
0.00235	0.0000726	30.91



The values of the molecular conductivity increase regularly with increasing dilution, but in neither case do these show much indication of approximating to a limit which would correspond to complete electrolytic dissociation of the polyiodide. The increase in the observed molecular conductivity may, however, not only be due simply to increased electrolytic dissociation of the polyiodides, for it is possible that on dilution the components of the solutions undergo dissociation of a non-electrolytic character. That changes do take place on dilution is shown by the experiments on the amounts of potassium iodide extracted from a given volume of aqueous solution by different quantities of nitrobenzene (p. 526) on addition of a constant quantity of iodine. Under the specified conditions, the amount of potassium iodide extracted by 50 c.c. of nitrobenzene is about 8 per cent. greater than that extracted by 20 c.c., which difference is probably due for the most part to changes undergone by the polyiodide in the nitrobenzene. A comparison of the conductivities of solutions having the same potassium iodide concentration, the iodine concentrations of which are, however, in the ratio of 4.5 : 1 (corresponding solutions in the above two tables), shows that the solutions containing the smaller quantity of iodine conduct approximately 10 per cent. better than those containing the larger quantity. This difference must be partly due to the difference in the viscosity of the two solutions and is scarcely sufficient to permit of any conclusions being drawn relatively to the nature of the components of the two solutions. Comparing the specific conductivities of these nitrobenzene solutions with aqueous solutions of binary potassium salts of the same concentration, we find that the former conduct approximately one-fifth as well as the latter, and must be considered as good conductors.

#### *Freezing Point Determinations.*

In our attempts further to elucidate the character of the solutions, some freezing point determinations were made, the results of which may be stated here. On account of experimental difficulties in the determinations, no quantitative conclusions can be drawn from the observations. One portion of nitrobenzene was distilled three times in a vacuum, another was purified by freezing out three times and distillation in a vacuum, but in each case the liquid obtained did not give a constant value for the freezing point in successive determinations. Under these circumstances, only very approximate measurements could be made. Iodine was dissolved in the purified nitrobenzene, the resulting solution containing about 40 grams per litre. A portion of this iodine solution was then shaken with potassium iodide until saturation was attained, and the solution thus obtained containing potassium iodide and iodine in molecular proportion

was poured off from the excess of solid matter. The concentration of the iodine and of the potassium iodide in this solution was 0.15 gram-molecule per litre. The freezing points of the pure nitrobenzene, the iodine solution, and the iodine-potassium iodide solution were then measured. The difference between the freezing points of the second and third solutions, taking the mean result of two series of determinations, was found to be about four-fifths of the difference between the freezing points of the pure nitrobenzene and the iodine solution. This relationship corresponds to a considerable dissociation of the triiodide which we suppose to be present in the solution.

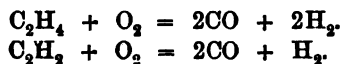
Although these measurements do not completely determine the nature of these interesting solutions, yet the solubility determinations indicate clearly the existence of complex periodides in the nitrobenzene solution. The high electrical conducting power points to electrolytic dissociation of these complex compounds existing in the solution, and the freezing point measurements indicate that dissociation takes place to a very considerable extent.

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## LVIII.—*The Slow Oxidation of Methane at Low Temperatures.*

By WILLIAM A. BONE and RICHARD V. WHEELER.

THE mode in which a hydrocarbon burns in a supply of oxygen insufficient to completely oxidise it to carbon monoxide (or dioxide) and steam has been the subject of much controversy. The view, at one time generally held, that under such conditions the hydrogen burns in preference to the carbon, can hardly be reconciled with the results of experiments on the explosion of ethylene or acetylene with less than an equal volume of oxygen (Lean and Bone, *Trans.*, 1892, 61, 873; Bone and Cain, *Trans.*, 1897, 71, 26). These results indicate that the main reaction in the explosion wave may be represented by such equations as



From these and other similar experiments, it is sometimes argued that in a limited oxygen supply the carbon of a hydrocarbon burns preferentially to the hydrogen; it should, however, be pointed out that the evidence supporting this contention is wholly derived from

investigations of the oxidation of hydrocarbons at the high temperatures of the explosion wave. The present paper records the results of experiments on the slow combustion of methane in an oxygen supply just sufficient to oxidise the carbon to carbon monoxide, at temperatures where the velocity of the reaction is just appreciable. This line of inquiry is, we believe, entirely new.

The reasons for the selection of methane as the most suitable hydrocarbon for these studies were as follows: (1) it is the simplest saturated hydrocarbon, and its molecule contains only one carbon atom, (2) preliminary experiments showed that it can be maintained at  $480^{\circ}$  to  $500^{\circ}$  (temperatures considerably higher than those afterwards employed in the oxidation studies) for many days without undergoing the least change, and (3) a mixture of two volumes of methane with one of oxygen is non-explosive. This was the mixture used throughout our experiments.

In a preliminary series of experiments, the object of which was to determine the most suitable experimental methods for the inquiry, the mixture of methane (2 vols.) and oxygen (1 vol.) was circulated through a tube containing fragments of unglazed porcelain maintained at a constant temperature (between  $400$  and  $450^{\circ}$ ) in a Lothar Meyer furnace. The apparatus involved, however, proved too complicated for experiments which necessarily extended over several days continuously; the results, it may be stated, indicated that a portion of the methane was burnt to carbon monoxide, carbon dioxide, and steam without any liberation of free hydrogen or carbon. We also tried maintaining the mixture at  $300^{\circ}$  to  $350^{\circ}$  in contact with palladium black, but the 'catalytic' effect of the metal introduced complications which made it difficult for us to follow the real cause of the reaction.\*

We finally resorted to the simple expedient of sealing the mixtures of methane and oxygen, under atmospheric pressure, in cylindrical bulbs of boro-silicate glass with capillary ends; the bulbs were afterwards maintained at constant temperatures (between  $300^{\circ}$  and  $400^{\circ}$ ) for several days in an air-bath, until the whole or a part of the oxygen had disappeared. The cooled bulbs were subsequently opened under mercury, any change in volume (always a contraction) noted, and the residual gas withdrawn for analysis. We were thus able to examine the gases at various periods during the oxidation of the methane at any given temperature, and we could hardly fail to detect the formation of a product at any stage of the oxidation which afterwards disappeared before the process was completed.

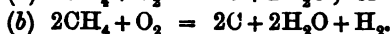
The interaction of two such gases as methane and oxygen in glass vessels at low temperatures being a surface phenomenon, the temperature

\* We desire to acknowledge our indebtedness to Mr. John Wilson, of the Battersea Polytechnic, for much valuable help in these preliminary experiments.

at which its velocity is just appreciable, as well as the velocity at any other given temperature, will, to a certain extent, depend on the character of the surface. In our experiments, 300° was the lowest temperature at which any interaction could be detected after the lapse of two or three weeks. At 325°, however, the velocity was much greater; at 350°, in some instances, the whole of the oxygen disappeared within three or four days, whilst at 400° the oxidation was always completed in a single day. But we have so far been unable to measure the relative velocities of the reaction at different temperatures on account of the fact that, except at 400°, when the velocity is considerable, the influence of the 'surface factor' may be very different even in two bulbs of the same size, shape, and material. Thus, between 325° and 350°, an appreciable amount of oxidation always occurred within three days, but of a series of similar bulbs filled with the same mixture and heated in the same bath, some exhibited a greater amount of oxidation in two or three days than others did in a week or more. Nor does the 'surface factor' of a given bulb remain constant over two or three successive experiments with the same mixture; whether it would finally become constant after a long series of experiments is a point we are now investigating.

It is of course impossible, by any means at our command, to determine the precise manner in which the methane molecule is attacked by the oxygen, but we are able to discover what is the first distinct *stage* of the reaction. This first stage may, obviously, involve one of three things, namely:

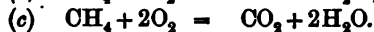
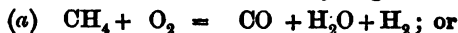
(1) Selective combustion of hydrogen, thus,



(2) Selective combustion of carbon, thus,



(3) Simultaneous oxidation of carbon and hydrogen, thus,



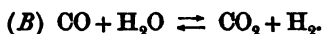
The primary oxidation products (which it will be seen may include carbon, hydrogen, carbon monoxide, carbon dioxide, and steam) may, however, react with each other, or with the original constituents of the mixture. We had therefore, as an important part of our inquiry, to investigate the possibilities of such reactions occurring in our bulbs at temperatures between 300° and 400°. We will now briefly discuss the evidence so obtained.

The possible secondary reactions may be classified as follows :

(A), those in which free carbon may be involved, for example :

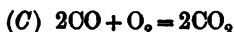


The evidence obtained shows that none of these reactions begin at temperatures between 300° and 400°.

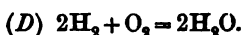


A series of experiments with bulbs similar to those used in the oxidation studies have shown that steam and carbon monoxide can be maintained at 325° for a fortnight without the slightest change occurring. At 350°, no action could be detected within a week, but after ten days some 1·7 per cent. of carbon dioxide had been formed ; at 400°, about the same amount of change occurred in a week. On the other hand, mixtures of equal volumes of hydrogen and carbon dioxide showed no signs of change when kept at 325° or 350° for a fortnight, or at 400° for a week.

The results of these experiments show that no complication arising from the interaction  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$  enters into any of our experiments on the oxidation of methane.



We have found that moderately dry carbon monoxide and oxygen do not react between 300° and 400°; the formation of between 0·7 and 1·7 per cent. of carbon dioxide could usually be detected when the *moist* gases were maintained at 325°, 350°, or 400° for a week. The effects of this possible secondary change in the methane experiments are therefore practically negligible.



In 1895, V. Meyer and Raum (*Ber.*, 28, 2804) published the results of an investigation on the combination of the elements of electrolytic gas in glass bulbs, very similar to those used by us, at temperatures between 300° and 518°. At 300°, the formation of water could just be detected after 65 days ; in the case of four out of five bulbs maintained at 350° for 5 days, a very small amount of combination occurred (between 0·5 and 1·9 per cent. only of the original gas had disappeared), whilst in the fifth bulb as much as 16·4 per cent. of the gases had combined.\* At 448°, the combination was still very slow. We have carefully repeated these experiments, using bulbs which had previously been employed for heating the mixtures of

\* Judging from our own experiments at this temperature, we are inclined to attribute this relatively large formation of water to some roughness of the inner surface of the bulb used either present originally or caused by a partial devitrification of the glass during the heating.

methane and oxygen. At  $335^{\circ}$ , we have never been able to detect the slightest formation of water from electrolytic gas within a week; at  $350^{\circ}$ , in six bulbs no combination took place in a week, although in the case of a seventh bulb, in which the glass had become devitrified at one end, the formation of water could be distinctly seen. At  $400^{\circ}$ , three bulbs exhibited no signs of change after three days; after a week, water could be distinctly seen in one bulb (nearly 40 per cent. of the mixture had combined), but none could be detected in the other two. Professor Dixon informs us that some years ago he maintained glass bulbs filled with electrolytic gas at  $350^{\circ}$  for several weeks, but was unable to detect any formation of water. Our own experience shows that hydrogen and oxygen, even when mixed in combining proportions and undiluted with other gases, do not within a week or two combine at  $350^{\circ}$  to any appreciable extent provided the glass surface with which the gases are in contact remains perfectly smooth. At  $400^{\circ}$ , however, we are on the border line where the formation of water may occasionally be recognised within a week, but hardly within three days; in our experiments with methane at this temperature, the whole of the oxygen always disappeared within a single day.

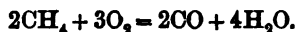
(E) We have also found that the following pairs of gases have no mutual action at temperatures between  $350^{\circ}$  and  $400^{\circ}$  (within a week or two). Methane and carbon dioxide; methane and steam; carbon monoxide and hydrogen.

It may therefore be taken for granted that no appreciable complication arising from possible secondary changes enters into our experiments on the oxidation of methane, the results of which may now be discussed.

We find that between  $300^{\circ}$  and  $400^{\circ}$  methane combines with oxygen with an enormously greater velocity than does hydrogen itself under the same conditions. We have followed the course of the oxidation in at least thirty cases, and although our mixtures never contained more than 1 volume of oxygen to 2 volumes of methane, *in no case have we been able to detect the liberation of free hydrogen or free carbon at any stage, from beginning to end, of the process.* The disappearance of oxygen was always accompanied, in the cooled products, by a corresponding diminution in volume, due to the formation of water. This formation of water could always be detected even in the initial stages of an experiment, when less than one-tenth of the oxygen originally present had disappeared; the amount of it increased as the oxidation proceeded, until the inner surface of the cooled bulb was completely wetted. Since these phenomena occurred at temperatures below that at which the elements of electrolytic gas combine (in similar bulbs) with any appreciable velocity, and since carbon dioxide and hydrogen do not react even at  $400^{\circ}$ , the natural

inference is that *water is one of the primary products of the partial oxidation of methane at these temperatures.*

At all stages of the oxidation, the gases in the bulbs contained (besides water vapour) carbon monoxide, carbon dioxide, unchanged methane, and, in some cases of course, oxygen. At no period have we been able to detect the formation of such products as methyl alcohol, formaldehyde, or formic acid; the carbon of that portion of the methane burnt always appeared in the products as carbon monoxide or dioxide. There was, however, no regularity in the ratio  $\text{CO}_2:\text{CO}$  at any given period of the oxidation, except towards the end; during the earlier period, it usually varied between 1:7 and 1:3, but finally it *approximated* to a value between 1:2 and 1:1. Since the influence of the reaction  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$  between  $300^\circ$  and  $400^\circ$  has been shown to be negligible, and that methane and carbon dioxide have no mutual action, our experiments point to the conclusion that *the first stage in the "partial" combustion of methane at low temperatures is a simultaneous oxidation of carbon and hydrogen to carbon monoxide and steam, thus:*



One curious feature about our results is the unexpectedly large proportion of carbon dioxide found in the gases at each stage, but especially towards the end of the oxidation. Now the rate at which carbon monoxide combines with oxygen, or reacts with steam, between  $300^\circ$  and  $400^\circ$  has been shown to be negligible; therefore we cannot explain the formation of any considerable quantity of carbon dioxide in an experiment on the supposition that carbon monoxide actually liberated during the primary oxidation is afterwards *gradually* transformed into the dioxide through the agency of steam and oxygen, or steam alone. The largest proportions of carbon dioxide were found in bulbs in which the mean rate of oxidation had been, for any particular temperature, fast; the two circumstances are, we are inclined to think, not unconnected. Further, we should perhaps state that our experiments suggest that the 'oxidation velocity' in a given case is accelerated after the first portions of the oxygen have disappeared, but this is a point which requires fuller investigation. We are inclined to take the following view of the formation of so much carbon dioxide. When the methane molecule is burnt, carbon monoxide and steam simultaneously come into being in an atmosphere containing oxygen. At the moment of their formation, these new molecules would be in an extremely labile and reactive condition, and it is probable that during this transitory 'labile period' a much more frequent exchange of oxygen would occur in the system  $\begin{array}{c|c|c} \text{CO} & \text{OH}_2 & \\ \text{CO} & \text{OH}_2 & \end{array} \text{O}_2$ , than under ordinary circumstances. It is also conceivable that the 'lability' of such

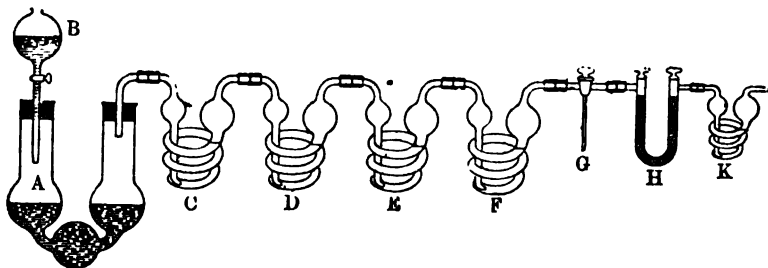
a system would be influenced by the rate at which the methane succumbs to the attack of the oxygen.

## EXPERIMENTAL.

### I.—*The Preparation of Pure Methane.*

The preparation of pure methane by Gladstone and Tribe's method is always a tedious process; if, however, an aluminium-mercury couple be substituted for the zinc-copper pair, the result is much more satisfactory. In fact, the action of the aluminium-mercury couple on a mixture of methyl iodide and alcohol is so energetic that the reaction vessel must be well cooled by immersion in iced water at the outset of the preparation, or otherwise the evolution of the gas becomes too rapid, and is difficult to control. In addition to being contaminated with the vapours of the alcohol and iodide, the gas almost invariably contains a small quantity (2 or 3 per cent.) of hydrogen. This may be easily

FIG. 1.



removed, after the other impurities have been eliminated, in one of two ways, namely: (1) by passing the gas through a layer of 'oxidised' palladium black at  $100^{\circ}$ , or (2) by liquefaction of the methane in a bulb immersed in liquid air, when, of course, the hydrogen passes on. The details of the method are as follows:

The central bulb of the Wöhler U-tube A (Fig. 1) is filled with clean aluminium foil, cut into pieces about one-eighth of an inch square. A few c.c. of a mercuric chloride solution are poured on to the foil which, in the course of a minute or two, becomes coated with mercury. The liquid is then drained off, and the couple rapidly washed (twice) with methyl alcohol. About 30 grams of methyl iodide are then poured on to the couple. The tap funnel, B, containing a mixture of 2 to 3 parts by weight of methyl iodide and one part of methyl alcohol, is quickly inserted in one limb of the U-tube by means of a rubber cork. The other limb is immediately connected with the arrangement for washing the gas, consisting of (1) the worm C surrounded by iced



water, (2) worms D and E containing a strong solution of sodium methoxide in methyl alcohol, and (3) worm F containing strong sulphuric acid. The lower part of A should be immersed in iced water; on dropping the mixture from B on to the couple, a good evolution of methane is obtained. The air is swept out of the apparatus through the vertical branch of the three-way tap, G, before connection with the apparatus for the elimination of hydrogen is made. When oxidised palladium sponge is used for this purpose, it is placed in the small U-tube, H, which is immersed in boiling water. The gas is afterwards dried by passing it through the worm, K, containing sulphuric acid. Where palladium sponge is not available, the removal of traces of hydrogen can be effected by means of liquid air, the methane condensing to a colourless liquid as fast as it is evolved.

We have frequently tested the purity of the gas so prepared by explosion analyses; the following are the results in the cases of four typical samples:

	(1).	(2).	(3).	(4).
Volume of gas taken ...	58.00	44.40	66.25	57.0
Contraction C .....	115.8	89.2	130.0	112.0
Absorption A .....	57.95	44.5	65.3	56.3

## II. *The Action of Heat on Methane.*

Since in the subsequent 'oxidation' experiments, mixtures of methane and oxygen were maintained at temperatures between 300° and 400° for, in some cases, as long as two or three weeks together, it was necessary to ascertain whether methane itself undergoes any change at temperatures at all near these limits. Accordingly, about 3 litres of pure methane were kept continuously circulating for six days and nights through a hard glass tube (about 0.75 metre long), packed with fragments of well-dried, unglazed porcelain, maintained at 480° in a Lothar Meyer furnace. In the circuit was a glass spiral, which, during the experiment, was kept surrounded by a freezing mixture. On examining the tube after the experiment, no blackening, or even discoloration of the porcelain, could be detected, nor could any liquid be seen in the glass spiral. The volume of the methane remained constant throughout the experiment, and analysis showed that it had undergone no change. Further experiments showed that only at 650—700° does methane begin to decompose, and even then very slowly.

## III.—*The Oxidation Experiments.*

The mixtures of methane and oxygen (the latter prepared by heating recrystallised potassium chlorate in hard glass bulbs, and afterwards washing it through a strong solution of potassium hydroxide) were

made in a graduated glass holder over pure strong sulphuric acid. The methane in each case was determined analytically by an explosion method, and the oxygen by absorption with strongly alkaline pyrogallol (freshly prepared). Altogether five mixtures were used; the percentage composition of each, leaving altogether out of account the small amount of nitrogen present (namely, 1.0, 2.16, 0.95, 3.6, and 2.67 per cent. respectively),\* is given below:

Mixture.	A.	B.	C.	D.	E.
Methane .....	69.0	66.66	67.44	66.80	66.90
Oxygen .....	31.0	33.34	32.56	32.20	33.10

*Filling of the Bulbs.*—The cylindrical Jena boro-silicate glass bulbs used in these experiments terminated at each end in a long capillary tube (1 mm. bore). They had a capacity of between 60 and 70 c.c. (length about 10 cm., diameter 3.5 cm.), except a few, somewhat larger (capacity 70 to 80 c.c.), used during the later stages of the research. Boro-silicate glass is eminently suited for the making of vessels in which gases are to be heated for long periods under pressure; in our own experiments the bulbs, filled at atmospheric pressure and temperature, could be maintained at 400° for, if necessary, many weeks without showing change in shape or capacity, or signs of devitrification. Similar bulbs made of ordinary soft or hard glass generally devitrified or burst when subjected to the same treatment. Further, boro-silicate glass possesses another great advantage over other kinds in that it withstands sudden changes of temperature.

Before being filled with the mixture under investigation, the inner surface of each bulb was thoroughly cleaned with hot strong nitric acid, and afterwards with distilled water. Each was subsequently dried in a current of hot air (dust free). A number of such clean, dry bulbs were connected in series, on the one hand, with the holder containing the mixture of methane and oxygen, and, on the other, through a drying tube to a Sprengel pump and manometer. When nearly vacuum, each bulb was strongly heated with a Bunsen burner and the exhaustion completed. As soon as the bulbs were cold, the mixture was admitted from the holder until the pressure in the apparatus was 2—3 mm. below the atmospheric; the capillaries of each bulb were then successively drawn out and sealed off in the blow-pipe.

*Heating of the Bulbs.*—The bulbs were heated, in batches of from 2 to 6 as required, in a special air-oven, the gas supply of which passed through a Stott's governor, and then through a Lothar Meyer regulator. The temperature was registered by a thermometer reading

\* In order to make the results of the various experiments strictly comparable, we propose to adopt this course throughout the paper in tabulating the composition of the various gaseous mixtures under discussion. Since the nitrogen in each case was taken 'by difference,' the tabulated results will always add up to 100.

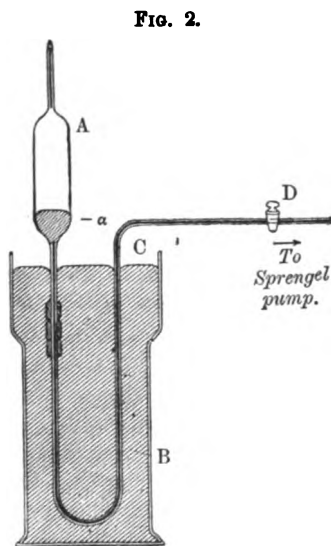
up to  $500^{\circ}$ , and we had no difficulty in keeping it practically constant for weeks together. The extreme variations on either side of the desired mean temperature were about  $5^{\circ}$  in the longest experiments; in the case of experiments extending over a few days only, the variations in temperature were even less.

*Examination of the Bulbs after Heating.*—As soon as each bulb was withdrawn from the air-bath, it was quickly cooled in water. The most superficial examination of the cold bulbs revealed two significant facts connected with the partial oxidation of the methane, namely, (1) no carbon had been deposited, and (2) the formation of a dew on the inner surface of the vessel. On standing such a bulb in a vertical position, the dew soon collected in the capillary as a colourless liquid.

The liquid was tasteless and odourless, it did not contain hydrogen peroxide, formaldehyde, or formic acid; it solidified in a freezing mixture, and the solid melted at  $0^{\circ}$ . It was, in short, water.

The bulbs were subsequently opened under mercury, and the gases withdrawn as follows:

A deep scratch having been made near the end of one of the capillaries of the bulb A (Fig. 2), the glass was nipped off under the surface of mercury contained in the cylinder, B. In each case, the mercury entered the bulb, partially filling it. After the lapse of half-an-hour, the level of the mercury inside the bulb ( $\alpha$ ) was marked (the levels inside and outside having been previously equalised). The open end



of the capillary was then forced into a stout rubber joint connected with the U-shaped capillary tube, C; the whole of this rubber joint and capillary had been previously filled with mercury as far as the tap D, through which connection was made with a Sprengel pump. All connections having been thoroughly exhausted, the tap, D, was opened, and the gas in A drawn off through the pump into tubes over mercury. Finally, the bulb, A, was detached, and its total volume, as well as the volume up to the mark  $\alpha$ , determined. In this way, the contraction, due to the formation of water during the oxidation, was approximately measured; in all cases, it corresponded to the volume of oxygen which subsequent analysis showed had disappeared.

*Analysis of the Residual Gases.*—The analysis of the residual gases constituted the most important part of the work, for on their accuracy depends the proof that no free hydrogen was formed during the course of the oxidation. The apparatus used was that described by one of us at a meeting of the Society in 1898 (Proc., 1898, 14, 154), and a long experience of its working has shown that it admits of a high degree of accuracy.

In addition to a large amount of unchanged methane, the gases always contained carbon dioxide, carbon monoxide, and in some cases oxygen also. The last three were removed and estimated in the following order, namely (1), carbon dioxide by means of a strong solution of potassium hydroxide, (2) oxygen by means of a freshly prepared and strongly alkaline solution of pyrogallol, and (3) carbon monoxide by means of freshly prepared ammoniacal cuprous chloride, the gas being afterwards treated with dilute sulphuric acid before remeasurement. When the gases contained more than 5 per cent. of carbon monoxide, they were subjected to a second treatment with a fresh portion of the cuprous chloride solution. A series of trial experiments satisfied us that practically the whole of the carbon monoxide in such a mixture can be removed in this way; certainly never as much as 0.5 per cent. remains unabsorbed.

After removal of the three foregoing constituents, a measured portion of the residual gas was exploded with a large excess of oxygen, and the contraction in volume ( $C$ ), and the absorption ( $A$ ) when the products of explosion were treated with potassium hydroxide, determined. It is essential to the accuracy of such an analysis that the explosive mixture ( $\text{CH}_4 + 2\text{O}_2$ ) should be largely diluted with excess of air, in order to avoid the oxidation of any nitrogen present, or deposition of carbon in the explosion vessel due to shock. In the case of these mixtures, we always added at least 100 volumes of diluents to every 50 to 60 volumes of the explosive mixture, and exploded the gases under half an atmosphere pressure. These precautions ensured the necessary conditions of accuracy.

From the ratio  $\frac{C}{A}$  obtained in any case, we were able to determine whether the gases exploded contained hydrogen in addition to methane. This ratio for pure methane is, of course, 2.0, and for mixtures of methane and hydrogen would be greater (thus it would be 2.015 for a gas containing 99 per cent. of methane, and 1 per cent. of hydrogen, and trial experiments have shown that this quantity of hydrogen can be detected with certainty). An examination of the results of twenty-five different experiments detailed in the following paragraphs will show that in sixteen cases the ratio fell between 1.99 and 2.00; in seven other cases, it lay between 1.95 and 1.99, whilst in

two cases only (2·007 and 2·005 respectively) was it higher than 2·00. These numbers, therefore, prove the absence of free hydrogen in the oxidation products at all stages of the process.

*Experiments at 300°.*

The rate at which methane and oxygen combine at this temperature is very slow, so that it is hardly ever possible to detect any change unless the heating be continued over two or three weeks. The results of two experiments, in both of which the formation of water could be distinctly seen, are given below. The mixture employed was A (methane = 69·0; oxygen = 31·0):

	Composition of dry gases after	
	14 days.	21 days.
Carbon dioxide .....	0·70	2·40
Carbon monoxide .....	3·85	6·40
Oxygen .....	27·10	21·40
Methane.....	68·35	69·80
<hr/>		
$\frac{C}{A}$ for residual gas exploded.....	1·97	2·00
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*Experiments at 325°.*

*First Series.*—Four bulbs filled, at 18° and 758 mm., with mixture D (methane = 66·8; oxygen = 33·2) and heated for 30 hours, 3, 6, and 11 days respectively. All showed the formation of water; it will be seen that more oxygen had disappeared in the bulb heated 3 days than in the one in which the action had continued over 6 days. The analytical results are given below:

Duration of heating.	30 hours.	3 days.	6 days.	11 days.
Carbon dioxide .....	nil	1·66	0·90	2·30
Carbon monoxide .....	1·07	7·24	4·35	7·45
Oxygen .....	31·60	24·10	28·45	23·25
Methane .....	67·33	67·00	66·30	67·00
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$\frac{C}{A}$ for residual gas } exploded .....	2·00	2·00	2·00	2·00
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*Second Series.*—Four bulbs filled, at 21° and 755 mm., with mixture E (methane = 66·9; oxygen = 33·1) and heated for 3, 7, 14, and 21 days respectively. Singularly enough, by far the greatest amount of interaction occurred in the bulb heated for 3 days; indeed, the order according to 'rate of oxidation' is nearly the reverse of that

according to the duration of the heating. These experiments afford a good illustration of the point emphasised in the introduction, namely, that the influence of 'surface factor,' in the case of several exactly similar vessels, upon the velocity of a gaseous reaction is often enormously different. The analytical results are as follows :

Duration of heating.	21 days.	14 days.	6 days.	3 days.
Carbon dioxide .....	2.07	1.40	2.00	12.85
Carbon monoxide .....	5.50	5.00	6.15	16.30
Oxygen .....	25.60	25.70	24.10	(2.00)*†
Methane.....	66.83	67.90	67.75	(68.85)
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$\frac{C}{A}$ for residual gas exploded.....	2.00	1.985	1.987	1.985
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*Experiments at 350°.*

*First Series.*—Three bulbs filled with mixture E (methane = 66.9 ; oxygen = 33.1) at 22° and 747 mm., and heated for 24 hours, 66 hours, and a week respectively. Analyses of residual gases gave following results :

Duration of heating.	24 hours.	66 hours.	7 days.
Carbon dioxide .....	0.35	0.38	14.0
Carbon monoxide .....	2.05	2.90	16.3
Oxygen .....	31.38	30.35	0.9
Methane .....	66.22	66.37	68.8†
<hr/>			
$\frac{C}{A}$ for residual gas exploded.....	1.98	1.99	2.00
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*Second Series.*—Three bulbs filled with mixture E at 21° and 755 mm., and heated for 1, 3, and 7 days respectively. We would draw attention to the fact that the bulb heated 7 days exhibited a much smaller amount of oxidation than the one heated for the same time in the previous experiment. The analytical results for the residual gases were as follows :

Duration of heating.	1 day.	3 days.	7 days.
Carbon dioxide .....	0.40	2.80	2.25
Carbon monoxide .....	2.15	8.95	4.90
Oxygen .....	31.40	21.80	26.60
Methane .....	66.05	66.45	66.25
<hr/>			
$\frac{C}{A}$ for residual gas exploded.....	2.00	2.00	1.995
<hr/>			

\* This number for oxygen is only approximate ; the same therefore applies to that given for methane.  
† See footnote, p 548.

*Third Series.*—Six bulbs filled with mixture B (methane = 66·6 ; oxygen = 33·3) maintained at 350° for 13 days. In each case, practically the whole of the oxygen had disappeared, and a large quantity of water was produced. The contractions, on opening the bulbs under mercury, amount to between 30 and 33 per cent. of the original volume. The products of four of the bulbs were analysed, with the following results ; attention is drawn to the large quantity of carbon dioxide produced in each case :

	(1).	(2).	(3).	(4).
Carbon dioxide .....	14·8	10·2	10·0	10·0
Carbon monoxide.....	16·0	23·6	21·5	22·2
Oxygen.....	nil	nil	0·3	nil
*Methane .....	69·2	66·2	68·2	67·8
<hr/>				
$\frac{C}{A}$ for residual gas exploded	2·007	1·994	2·005	1·956
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#### *Experiments at 400°.*

At this temperature, methane is rapidly oxidised, and differences due to surface factor in a series of similar bulbs tend to disappear. We have always found that the oxygen in our mixtures disappeared within a single day, and that the phenomena were altogether more regular than at lower temperatures. We would in this connection again point out that we have maintained bulbs containing electrolytic gas at 400° for 3 days, and in many cases a week, without finding any appreciable formation of water. The following are the analytical results from an experiment in which five bulbs filled with mixture C (methane = 67·44 ; oxygen = 32·56) at 20° and 750 mm. were heated for 1, 2, 4, and 11 days (two bulbs) respectively. The contraction observed on opening these bulbs under mercury amounted to as nearly as possible one-third of the original volume :

Duration of heating.	1 day.	2 days.	4 days.	11 days.	11 days.
Carbon dioxide .....	11·4	12·4	11·3	10·6	11·9
Carbon monoxide .....	18·4	17·0	17·6	18·9	18·6
*Methane .....	70·2	70·6	71·1	70·5	69·5
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$\frac{C}{A}$ for residual gas exploded	1·95	1·99	2·00	2·00	2·00
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\* The percentage of methane in these products, and also in nearly all other experiments in which a large proportion (over 10 per cent.) of carbon dioxide was produced, is rather higher than it should be. We have reason to believe that this is caused by a small absorption of carbon dioxide by the alkali in the glass,

We are continuing this work and extending it to other hydrocarbons.

In conclusion, we desire to state that the expenses of this research have been defrayed out of grants received from the Government Grant Committee of the Royal Society.

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MANCHESTER.

### LIX.—*Derivatives of $\alpha$ -Aminocamphoroxime.*

By ARTHUR LAPWORTH and ALFRED WILLIAM HARVEY.

It is a point of some theoretical interest that most  $\alpha$ -substituted camphors are not capable of affording oximes, although when the substituents are present in other positions, that inability is not observed. Hitherto, exceptions to this general rule have been noticed with  $\alpha$ -hydroxycamphor (Manasse, *Ber.*, 1897, 30, 668),  $\alpha$ -isonitrosocamphor (*Ber.*, 1894, 26, 243), and Reyhler's camphorsulphonic acid (*Bull. Soc. Chim.*, 1898, [iii], 19, 120). Substituted camphoroximes have also been prepared from  $\pi$ -bromocamphor (Kipping and Revis, *Proc.*, 1896, 12, 77) and from  $\beta$ -bromo- and  $\beta$ -chloro-camphor (Forster, *Trans.*, 1902, 81, 268).

We have found that  $\alpha$ -aminocamphor constitutes another exception to the above-mentioned rule, as it yields an oxime without difficulty if proper precautions are taken.

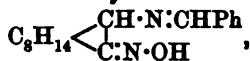
The study of camphoroxime, which has engaged the attention of several chemists, has presented points of more than ordinary interest in consequence of an extremely labile character of the molecule which the substituted camphoroximes do not appear to possess.  $\alpha$ -Aminocamphoroxime, however, might be expected to exhibit certain peculiarities of its own, more especially as the oximes of the type  $R \cdot C \begin{smallmatrix} \nwarrow NH_2 \\ \nearrow N \cdot OH \end{smallmatrix}$  are known to yield a variety of interesting ring compounds on treatment with anhydrides, aliphatic aldehydes, &c.

$\alpha$ -Aminocamphoroxime is much more susceptible to alkaline hydrolysis than is camphoroxime itself, and is not easily prepared from  $\alpha$ -aminocamphor by the use of an alkaline solution of hydroxylamine. By employing hydroxylamine acetate in presence of a large excess of or a 'condensation' of carbon dioxide on the glass surface. Such an absorption, or condensation, would make the methane appear *proportionately* higher in the products, since it was in all cases taken as the 'difference' between the total volume of (nitrogen free) gas analysed, and the sum of the carbon dioxide, carbon monoxide, and oxygen found.



sodium acetate, however, the oxime may be obtained without difficulty in large amount.

The substance has the properties both of an amine and of an oxime ; it dissolves readily in dilute acids and in excess of alkalis, forms definite salts with acids, and yields crystalline metallic derivatives. It affords a beautiful, crystalline dibenzoyl derivative,  $C_8H_{14} \begin{matrix} \diagup CH \cdot NH \cdot COpH \\ \diagdown C : N \cdot O \cdot COpH \end{matrix}$ , and reacts with one mol. of potassium cyanate to give a well-defined carbamide. In accordance with the fact that it contains both an amino- and a hydroxyl group, it combines with two mols. of phenylcarbimide. When warmed with benzaldehyde, the amino-group reacts in the normal manner and a monobenzylidene derivative,

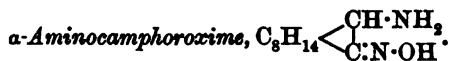


is produced.

Aminocamphoroxime shows no tendency to become converted into a campholenonitrile (compare Forster, *Trans.*, 1902, 81, 268), and on treatment with acetic anhydride is converted into a well-defined crystalline compound, which is perhaps the analogue of the compound obtained under similar circumstances from benzenylamidoxime, that is to say a ring compound of the azoxime type.

It was originally the intention of one of us to investigate these products and also to determine whether  $\alpha$ -amino- and  $\alpha$ -hydroxycampholenonitriles would break down with alkalis as camphanonitrile was found to do (Lapworth and Lenton, *Trans.*, 1901, 79, 1292), but as we hear privately from Dr. Forster that he has for a long time contemplated an extensive examination of substituted camphoroximes, the work has been abandoned in his favour.

#### EXPERIMENTAL.



Ordinary aminocamphor may be converted into its oxime by the use of hydroxylamine in the presence of a large excess of cold concentrated sodium hydroxide, and the amount of oxime produced may frequently be considerable. This method was the one which we at first employed, but in very many cases in which we attempted to deal with more than 5 grams of material at a time, it was found that the yield of oxime was very poor, and we did not succeed in discovering what were the necessary conditions. In some cases, the experiments were perfectly satisfactory, whilst in others, in which the conditions and concentrations employed appeared to be exactly similar, the reverse was the case.

However, by using an aqueous solution of hydroxylamine hydrochloride containing a large excess of sodium acetate, the results were more consistent. The following is the mode of treatment which we have finally adopted, and by means of it the oxime may be prepared in considerable quantities at a time.

Aminocamphor hydrochloride (5 grams), hydroxylamine hydrochloride (3 grams), and sodium acetate (12 grams) are dissolved in water (20 c.c.) and heated on the water-bath for 4—6 hours. The liquid is then cooled and separated by filtration from any insoluble matter which may have appeared. As the precipitation of the impure oxime from an acid solution such as this frequently causes its deposition as a viscid oil, it is better, at this stage, to pour the liquid, with constant stirring, into excess of 10 per cent. sodium hydroxide solution (about 50 c.c.). To the resulting clear liquid, dilute hydrochloric acid is added drop by drop until the white material which separates no longer increases in amount. After 10 minutes, the solid matter is separated by filtration and well washed with water. A further quantity of oxime may usually be obtained from the mother liquor by suitable treatment with acids or alkalis. The yield is about 50—60 per cent. of the theoretical. The dried oxime, which presents the appearance of a bulky mass of minute plates, may be purified by crystallisation from hot benzene. On analysis :

0.1475 gave 0.3563  $\text{CO}_2$  and 0.1344  $\text{H}_2\text{O}$ .  $\text{C} = 65.9$  ;  $\text{H} = 10.1$ .

0.2270 „ 31.1 c.c. moist nitrogen at  $20^\circ$  and 761 mm.  $\text{N} = 15.9$ .

$\text{C}_{10}\text{H}_{18}\text{ON}_2$  requires  $\text{C} = 65.9$  ;  $\text{H} = 9.9$  ;  $\text{N} = 15.4$  per cent.

The oxime dissolves somewhat readily in ethyl or methyl alcohol, ethyl acetate, acetone, benzene, chloroform, or carbon tetrachloride, but is practically insoluble in cold water or light petroleum. It crystallises badly from most organic solvents, with the exception of benzene, from which it separates in thin, flaky plates or in flattened prisms. It melts sharply at  $144$ — $145^\circ$ . The pure, dry substance, when slightly warmed, becomes very easily electrified by friction.

The smaller crystals are well-formed, six-sided plates, which belong, in all probability, to the rhombic system. When carefully heated on a glass slip beneath a cover-glass, the oxime sublimes slightly in similar forms ; after melting, it solidifies rapidly to aggregates of well-formed, elongated plates, the surfaces of which are, for the most part, parallel to the axial plane, but here and there, in convergent polarised light, the axis of a biaxial figure of wide angle may be observed ; here, the double refraction is negative.

The oxime and its derivatives are optically active. A 1 per cent. solution of the oxime in absolute alcohol had  $[\alpha]_D$   $60.5^\circ$  at  $18^\circ$ .

In order to observe the rotation of the ion in aqueous solutions of

the salts of the oxime, a 1 per cent. solution of the oxime in dilute hydrochloric acid was examined ; excess of hydrochloric acid produced no marked effect on the rotation. The solution had  $[\alpha]_D 36.7^\circ$  at  $16^\circ$ , giving for the ion  $[\alpha]_D 36.5^\circ$ .

The substance has both acidic and basic properties, dissolves readily in dilute mineral acids and in a large quantity of alkali. On adding acid to its solution in alkalis, the oxime is almost completely precipitated, whilst the liquid remains strongly alkaline. It forms sodium and potassium salts, but these are only obtained crystalline in presence of a large excess of strong alkali, and have not been closely examined.

The compound, when gently heated above its melting point, emits a faint odour resembling that of camphoroxime. At still higher temperatures, profound decomposition occurs, and water and gases with an ammoniacal odour are evolved, whilst a waxy substance, with an odour resembling that of camphenone, distils.

*Aminocamphoroxime hydrochloride*,  $C_{10}H_{18}ON_2 \cdot HCl \cdot H_2O$ , is prepared by dissolving the oxime in the requisite quantity of hot 15 per cent. hydrochloric acid. It crystallises, as the solution cools, in flat, rectangular prisms, is very readily soluble in ethyl or methyl alcohol, and still more so in water. The water of crystallisation could not be determined directly owing to the instability of the substance when heated. It contains  $1H_2O$ , as the following facts indicate :

0.3071 contained 0.0460 Cl.  $Cl = 15.0$ .

$C_{10}H_{18}ON_2 \cdot HCl \cdot H_2O$  requires  $Cl = 15.0$  per cent.

Moreover, its specific rotation in 2 per cent. aqueous solution was  $[\alpha]_D 27.6^\circ$ , whilst from the observations above recorded the calculated number for the monohydrated salt is  $[\alpha]_D 28.3^\circ$ .

The majority of the other salts of the oxime, such as the sulphate, nitrate, picrate, ferro- and ferri-cyanide, and the aurichloride, are very soluble in water and are not very characteristic.

The *platinichloride*,  $(C_{10}H_{18}ON_2)_2 \cdot H_2PtCl_6$ , is precipitated in the form of minute, yellowish-grey needles on mixing strong solutions of the hydrochloride and chloroplatinic acid. It is readily soluble in water, dissolves slowly in hot alcohol, and may be precipitated from its alcoholic solution by addition of ether as long, yellow needles which melt and decompose at  $209-211^\circ$ . The extinction in polarised light is straight; the double refraction is strong, and the directions of greatest elasticity and length are at right angles :

0.1639 gave 0.0398 Pt.  $Pt = 24.3$ .

$(C_{10}H_{18}ON_2)_2 \cdot H_2PtCl_6$  requires  $Pt = 25.2$  per cent.

*Dibenzoylaminocamphoroxime*,  $C_8H_{14} \begin{array}{l} \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{C} : \text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \end{array}$  :—This sub-

stance is formed when aminocamphoroxime is dissolved in a considerable excess of 10 per cent. sodium hydroxide solution, and subjected to the action of benzoyl chloride in the usual manner, the temperature of the mixture being kept low by the addition of powdered ice. The white, oily mass which is deposited may be collected by means of a glass rod, and, after drying, triturated with absolute alcohol, when it rapidly becomes pulverulent, and may be drained on porous earthenware and crystallised from absolute alcohol. On analysis :

0.2708 gave 0.7354  $\text{CO}_2$  and 0.1656  $\text{H}_2\text{O}$ .  $\text{C} = 74.0$ ;  $\text{H} = 6.8$ .

$\text{C}_{24}\text{H}_{26}\text{O}_3\text{N}_2$  requires  $\text{C} = 74.2$ ;  $\text{H} = 6.7$  per cent.

The compound is somewhat readily soluble in methyl or ethyl alcohol, ethyl acetate, or acetone, much less readily so in ether or benzene, and is nearly insoluble in light petroleum. It is best crystallised from ethyl alcohol, from which it separates in brilliant, transparent prisms, which are often of considerable size and probably belong to the rhombic system. Rapidly recrystallised, it forms minute, compact prisms. It melts sharply and without decomposition at  $146-147^\circ$ , and solidifies on cooling very slowly, unless the temperature is kept at about  $120^\circ$ .

When crushed fragments of the crystals are observed in convergent polarised light, a biaxial interference figure may occasionally be seen. The double refraction is strong and positive in sign.

The rotatory power was determined in absolute alcohol. 0.3317 gram dissolved in 25.1 c.c., gave  $\alpha_D$   $2.77^\circ$  in a 2-dm. tube at  $18^\circ$ , hence  $[\alpha]_D$   $104.8^\circ$ .

Attempts to prepare an acetyl derivative of the oxime were unsuccessful. Treatment with acetyl chloride converts the substance into a mixture, of which a part is soluble in water and the remainder is oily and has resisted all attempts at purification. Acetic anhydride acts violently on the oxime, affording a small quantity of a crystalline compound which evolves acetic acid when warmed with sulphuric acid.

The carbamide,  $\text{C}_8\text{H}_{14} \begin{matrix} \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2 \\ | \\ \text{C} : \text{N} \cdot \text{OH} \end{matrix}$ .—This is easily prepared

by adding a solution of potassium cyanate to one of the hydrochloride of the oxime, and warming the mixture on the water-bath for 15 minutes, when it separates as a bulky mass of minute needles which may be purified by crystallisation from methyl alcohol. A specimen was analysed :

0.2641 gave 0.5664  $\text{CO}_2$  and 0.2004  $\text{H}_2\text{O}$ .  $\text{C} = 58.2$ ;  $\text{H} = 8.4$ .

$\text{C}_{11} 19\text{O}_2\text{N}_8$  requires  $= 58.6$ ;  $= 8.4$  per cent.

The compound is readily soluble in acetone or ethyl alcohol, less

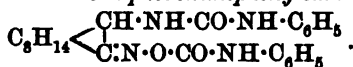
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readily so in ethyl acetate or methyl alcohol, and dissolves only sparingly in chloroform, carbon tetrachloride, benzene, or light petroleum. It is most conveniently crystallised from methyl alcohol, from which it separates in two entirely different forms according to the conditions. If the hot concentrated solution is cooled rapidly, the compound frequently appears as a bulky or flocculent mass of slender needles, whilst if the solution is allowed to cool very slowly, or if dilute ethyl alcohol is the solvent, the substance is usually deposited in the form of large, transparent, six-sided plates, but it is not always possible to ensure the deposition of either form at will. The melting point of the two forms appears to be the same, namely,  $203-204^{\circ}$ , when complete decomposition ensues; on one occasion, however, a specimen of the plate-like form was seen to fuse at  $158-159^{\circ}$ , and, solidifying immediately, melted once more at  $203-204^{\circ}$ ; this would appear to indicate that, on heating, one form undergoes conversion into the other, but we have not been able to obtain satisfactory confirmation of this view.

A solution of the compound in hot benzene forms a transparent jelly on cooling and could not be made to deposit crystals.

The rotatory power was determined in absolute alcohol, 0.2333 gram being dissolved in 25 c.c. of the solvent, and was found to be  $[\alpha]_D^{40.9^{\circ}}$  at  $14^{\circ}$ .

The *phenylcarbamide of camphoroximephenylcarbamate*,



—Aminocamphoroxime (3.8 grams) is suspended in absolute ether and treated with phenylcarbimide (5 grams) dissolved in the same liquid. Immediate combination occurs with formation of a white, very sparingly soluble material, which may be separated by filtration and purified by crystallisation from a large bulk of methyl alcohol. On analysis :

0.2266 gave 0.5716  $\text{CO}_2$  and 0.1381  $\text{H}_2\text{O}$ . C = 68.8; H = 6.8.

$\text{C}_{24}\text{H}_{28}\text{O}_3\text{N}_4$  requires C = 68.6; H = 6.7 per cent.

$\text{C}_{17}\text{H}_{28}\text{O}_3\text{N}_3$  „ C = 67.7; H = 7.6 „

The substance, which, as analysis indicates, is evidently the product of union of two molecules of the phenylcarbimide with one of the amino-oxime, is readily soluble in ethyl acetate, acetone, or ethyl alcohol, less readily so in methyl alcohol or benzene, and is very sparingly soluble in ether or light petroleum. It crystallises from hot absolute alcohol in long, slender prisms, and from hot methyl alcohol in bulky masses of asbestos-like needles. It melts at  $175-177^{\circ}$  and does not solidify on cooling. The crystals from absolute alcohol have straight extinction in polarised light, the directions of greatest elasticity

being coincident with their length; the double refraction is strong. For the determination of its optical activity, 0.2603 gram was dissolved in 25 c.c. of absolute alcohol, and this solution, examined in a 2-dcm. tube at  $15^\circ$ , gave  $\alpha_D - 1.18^\circ$ , whence  $[\alpha]_D - 56.6^\circ$ .

The *benzylidene* compound,  $C_8H_{14} \begin{matrix} \text{CH} \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_5 \\ \text{C} : \text{N} \cdot \text{OH} \end{matrix}$ .—Molecular proportions of the oxime and benzaldehyde are dissolved in a small quantity of alcohol and warmed on the water-bath for 4 hours. At the end of this time, the mixture is cooled and the crystals separated and crystallised once or twice from hot methyl alcohol; a further quantity of material may be obtained from the mother liquor by dilution with water. On analysis :

0.3290 gave 0.9085  $\text{CO}_2$  and 0.2390  $\text{H}_2\text{O}$ . C = 75.4; H = 8.1.

$C_{17}H_{22}ON_2$  requires C = 75.6; H = 8.2 per cent.

The compound dissolves somewhat readily in ethyl or methyl alcohol, ethyl acetate or acetone, less readily in benzene, chloroform, or carbon tetrachloride, and is insoluble in light petroleum. It separates from alcohol in brilliant, transparent, apparently hemihedral prisms, closely resembling those of magnesium sulphate. It melts at  $153\text{--}154^\circ$  and on cooling solidifies very slowly, melting afterwards at the same temperature.

The crystals are probably rhombic, have straight extinction in polarised light and are strongly doubly refractive. Melted on a glass slide beneath a cover-slip, the substance slowly sets to a mass of well-formed plates, which usually show straight extinction; through some, however, the optic axis of a biaxial interference figure of wide angle emerges obliquely through the field.

The compound is nearly insoluble in dilute sodium hydroxide solution, but dissolves readily in dilute hydrochloric acid, being precipitated from the solution on addition of alkali. When warmed for a few minutes with moderately concentrated acid, it suffers hydrolysis, yielding benzaldehyde and the original amino-oxime.

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## LX.—*The Absorption Spectra of Metallic Nitrates.*

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### *Part I.*

A BAND of absorption was discovered by Soret in nitric acid and potassium nitrate, but in ethyl nitrate examined by Soret and Rilliet it did not appear. In 1887, I made an extended examination of the absorption spectra of those nitrates of simplest constitution, such as nitric acid, and potassium, sodium, silver, and thallium nitrates, chiefly with the object of ascertaining definitely whether there was any difference in the absorption spectra transmitted by these salts both in strong and in dilute solutions. They were selected because the band which is characteristic of them is situated in the ultra-violet region; they are anhydrous, are derived from monad metals, and there are great differences in the atomic masses of the metals which enter into their composition, for instance,  $H = 1$ ,  $Na = 23$ ,  $K = 39$ ,  $Ag = 108$ ,  $Tl = 204$ . The results which immediately followed are stated under the head of *1st Series*. In 1898, I returned to the subject and the results obtained are in part described under *2nd, 3rd, 4th, and 5th Series*. The method of examination was precisely the same as that pursued with organic substances. As many, if not all, of the photographs taken at that time are still in existence, I have recently re-examined them and find that in the earlier stages of the work the simple cadmium spark spectrum was used as the source of rays, but that the mode of examination recorded in detail in "*The Absorption Spectra of the Alkaloids*" was afterwards adopted (see *Phil. Trans.*, Part II, 1885). Subsequently the lead, tin, and cadmium alloys were modified and improved by the introduction of bismuth. There were thus photographed from these electrodes 153 sharply defined metallic lines of nearly the same intensity, distributed fairly equally throughout the whole spectrum, which was 3.95 inches in length, and, if necessary, capable of being enlarged to 25 diameters. In addition to the metallic lines, which are definite fixed points in the spectrum, there was a background of continuous rays filling up the spaces between them. For the extreme ultra-violet about wave-length 2000, electrodes of indium and of copper were used for the purpose of filling up the spaces between the cadmium lines.

Seven different series of experiments have been made on different metallic nitrates, chiefly on those which afford colourless solutions. The term colourless is here used in the ordinary acceptation of the term, that is, no colour could be perceived by the eye when viewing the solutions in the usual manner.

*1st Series.*—A decigram-molecular weight of each of the four following substances, nitric acid, potassium, silver, and thallium nitrates was made up to a given volume with pure distilled water. The three former were made up to a volume of 40 c.c., but thallium nitrate, being less soluble, was contained in 400 c.c. The solutions were examined in cells of a thickness of 25 mm. down to 1 mm., in the case of thallium nitrate from 50 mm. to 2 mm.

The solutions were then successively diluted down to 1 decigram-molecule in 5000 c.c., at which dilution it was expected that the coefficient of extinction of absorption would be attained.

As the thallium solution is 1/10th the strength of the others, 50 c.c. were reckoned as equivalent to 5 c.c. of them.

A description of the absorption spectra at different stages here follows, the measurements being expressed both in oscillation-frequencies and wave-lengths.

The diagram on p. 558 shows the most characteristic portion of the curves, which were plotted in the usual manner as in the investigation of organic compounds.

In explanation of the diagram, the following notes are appended.

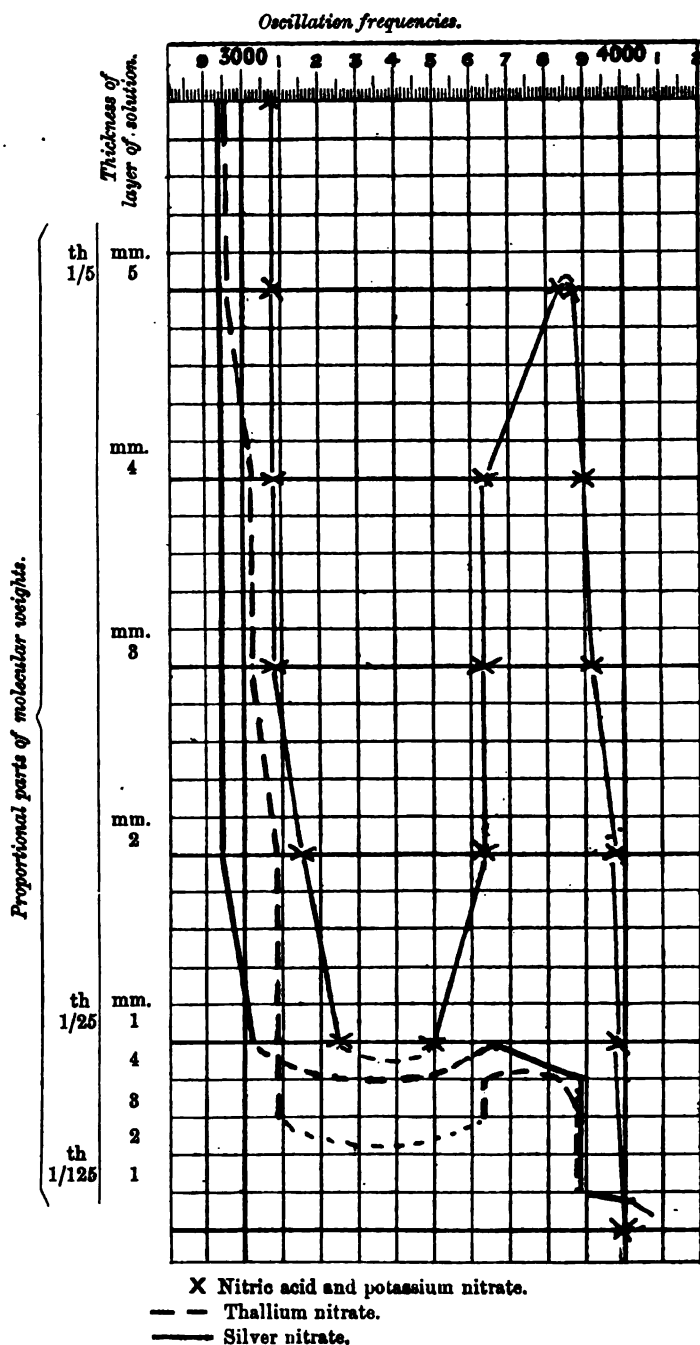
Standard of volume 40 c.c. The weight of substance contained in 40 c.c. when viewed through different thicknesses which are specified, or in the case of thallium nitrate, which is less soluble, through equivalent thicknesses, is shown below :

<i>1st Series.</i>	HNO <sub>3</sub> . grams.	KNO <sub>3</sub> . grams.	AgNO <sub>3</sub> . grams.	TlNO <sub>3</sub> . grams.
1st dilution { 5 mm.	1.26	2.02	3.38	5.32
{ 1   ,,	0.252	0.404	0.672	1.064
2nd dilution 1 mm.	0.0504	0.0808	0.1344	0.2128
Molecular proportions	63	101	169	266

With regard to 40 c.c., it may be remarked that it was found by experience to be a convenient standard to work with, since in the cells which were used it is a volume which very nearly occupies a cube, and consequently linear measures of the layers of liquid examined represent proportional weights or molecular proportions of the dissolved salt in the path of the rays.

These curves are such as I have previously described as curves of molecular vibrations.





1st Series.—Nitric Acid.  $\text{HNO}_3$ , 6.3 grams dissolved in water and diluted to 40 c.c.

Thickness of layer of liquid.	25 mm.		20 mm.		15 mm.		10 mm.		5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to.....	2998	3840	3008	3824	3008	3824	3066	3261	3087	3238	3087	3238	3087	3238	3151	3171	3256	3072
Absorption band.....									3087	3238	3087	3238	3087	3238	3087	3151	3256	3072
Rays transmitted to .....									to	to	to	to	to	to	to	to	to	to
									3896	2564	3674	2740	3647	2740	3647	2740	3507	2852
									a line	2564	3896	2564	3919	3549	2528	2528	3988	2507
									generally									
$\text{HNO}_3$ , 6.3 grams in 200 c.c.																		
Spectrum extends to .....									3256	3072	3988	2507	3988	2507	3988	2507	4055	2466
Absorption band .....									3256	3072								
Rays transmitted to .....									3507	2852								
									3988	2507								
$\text{HNO}_3$ , 6.3 grams in 1000 c.c.																		
Rays transmitted to .....									4055	2466	4055	2466	4055	2466	4146	2411	4146	2411
$\text{HNO}_3$ , 6.3 grams in 5000 c.c.																		
Rays transmitted to .....									4146	2411	4269	2343	4269	2343	4351	2299	4347	2302

A solution of Potassium Nitrate containing the same quantity of  $\text{NO}_2$  in 40 c.c. as this solution of nitric acid, gave exactly the same spectrum at all similar dilutions.

1st Series.—*Silver Nitrate.*  $\text{AgNO}_3$ , 16.9 grams in 40 c.c.

Thickness of layer of liquid .....	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to.....	2941	3403	2941	3403	2941	3403	2941	3403	3008	3324
Absorption band indicated.							a strong line at		a strong line at	
Ray transmitted at .....							3647	2740	3647	2740

$\text{AgNO}_3$ , 16.9 grams in 200 c.c.

Spectrum extends to.....	3008	3324	3896	2564	3896	2564	3896	2564	3896	2564
Ray transmitted at .....	3647	2740								

$\text{AgNO}_3$ , 16.9 grams in 1000 c.c.

Spectrum extends to.....	3896	2564	4028	2482	4028	2482	4028	2482	4028	2482
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The transmission of an isolated strong line indicates the position of a feeble band of absorption lying between it and the continuous spectrum, also that the absorption is greatly weakened and is beginning to fade away. This remark applies to the descriptions of other spectra which will follow.

$\text{AgNO}_3$ , 16.9 grams in 5000 c.c.

Spectrum extends to.....	4028	2482	4066	2459	4066	2459	4066	2459	4351	2299
--------------------------	------	------	------	------	------	------	------	------	------	------

1st Series.—*Thallium Nitrate, TlNO<sub>3</sub>, 26.6 grams in 400 c.c.*

Thickness of layer of liquid.....	50 mm.		40 mm.		30 mm.		20 mm.		10 mm.		8 mm.		4 mm.		4 and 2 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to .....	2949	3398	3008	3324	3008	3324	3080	3245	3080	3245	3080	3245	3080	3245	3896	2564
Absorption band .....									3080 to 3647	3245 to 2740	3080 to 3647	3245 to 2740	3080 to 3896	3245 to 3564	"	"
Rays transmitted at .....									3647	2740	3855	2593	3896	3564	"	"

TlNO<sub>3</sub>, 26.6 grams in 1000 c.c.

	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Spectrum extends to .....	3896	2564	4028	2482	4028	2482	4055	2466	4055	2466

TlNO<sub>3</sub>, 26.6 grams in 5000 c.c.

	4055	2466	4109	2434	4141	2415	4141	2415	4206	2378
Spectrum extends to .....										

It will be remarked that the absorption curves of nitric acid and potassium nitrate are identical in every particular, whilst those of silver and thallium nitrates are somewhat different, not only from that of nitric acid, but each differs from the other. The salts with high molecular weights are those which exhibit the greater extent of absorption, and moreover the absorption band extends further towards the less refrangible rays. The loading of the molecule produces a similar effect in organic substances as is now well known.

*2nd Series.*—Normal solutions of nitrates were made and examined through a uniform thickness of 200 mm., the solutions being diluted successively through 1/2, 1/4, 1/20, 1/100, 1/200, 1/300, 1/400, 1/500, 1/600, 1/700, 1/800, 1/900, and 1/1000 volumes of water. The final dilution may be expressed as a gram-molecular weight of the substance contained in 1000 litres.

It was necessary to carry the dilutions thus far in order to ascertain whether or no a second absorption band occurred in the region of rays more refrangible than those absorbed by nitric acid, since a band might be introduced by the metallic element of the salt. The following measurements are recorded in oscillation frequencies only, which are the reciprocals of the wave-length numbers.

*2nd Series.—Nitric Acid.*

Normal solution ; 63 grams per litre. Column of liquid 200 mm.

Dilution.	Spectrum continuous to $\frac{1}{\lambda}$ .		
1/1	2884.		
1/2	2884.		
	A line at 2938.		
1/4	2884.		
	Line at 2938.		
1/20	3004.	<b>Absorption Band.</b>	<b>Rays transmitted.</b>
	Line feeble 3069.	$\frac{1}{\lambda}$ .	$\frac{1}{\lambda}$ .
1/100	3155.	3069 to 3842.	Line at 3842.
1/200	3155.	3155 to 3504.	3504—3902.
1/800	The same as 1/200, but absorption band less marked.	3155 to 3504.	3504—3940.
	Rays transmitted to		4050.
1/400 to 1/900	The same.		
	Spectrum ends at		4050.

*2nd Series.—Potassium Nitrate.*

Normal solution ; 23.1 grams in 200 c.c. Various dilutions ; 200 mm.

Dilution.	Spectrum continuous to $\frac{1}{\lambda}$ .		
1/1	2884.		
1/2	2884.		
	Line very feeble 2938.		
1/4	2884.		
	Line stronger 2938.		
1/20	2884.		
	Lines very feeble 3004—3062	<b>Absorption Band.</b>	Just visible 3836.
		$\frac{1}{\lambda}$ .	
1/100	3155.	3155 to 3504.	3504 to 3905.
	Lines very feeble 3308 and 3341		
1/200	3062	Rays feebly transmitted to 3504.	3504 to 3894.
1/300 to 1/900	The same, a weakness seen between 3062 and 3471.		
	Spectrum ends at		4034.

*2nd Series.—Silver Nitrate.*

Normal solution ; 33.98 grams in 200 c.c. Various dilutions ; column of liquid, 200 mm. in thickness.

Dilution.	Spectrum continuous to $\frac{1}{\lambda}$ .		
1/1	2813.		
1/2	2884.		
1/4	2938.		
1/20	3004.	<b>Absorption band.</b>	
	Line feeble 3069.	$\frac{1}{\lambda}$ .	
1/100	3149.	3149 to 3836.	Line visible at 3836.
1/200	3149.	3149 to 3504.	3495 to 3940.
1/300	3149.	The same.	3495 to 3940.
1/400	The band has disappeared, rays continuous to		
1/500 to 1/1000	The same, rays continuous to		
			4034.
			4120.

This solution was brilliantly clear and it remained five days exposed to diffused sunlight without becoming opalescent or discoloured in the slightest degree,

*2nd Series.—Silver Nitrate.*

Normal solution diluted. Column of liquid, 200 mm.

Dilution.	Spectrum continuous to $\frac{1}{\lambda}$ .		
1/1	2813.		
1/2	2884.		
1/4	2988.		
1/20	3004.		
	A line at 2938.	<b>Absorption band.</b>	
1/100	3149.	$\frac{1}{\lambda}$ .	Line visible 3836.
1/200	3149.	<b>3149 to 3504.</b>	Rays transmitted 3495 to 3940.
		The same.	3495 to 3940.
1/800	3149.	Absorption complete.	
1/400	4034 rays continuous, absorption band ceases.		
1/500 to 1/900	The same, with the spectrum becoming stronger.		
1/1000	Rays continuous to 4120.		
	Water transmits to $\frac{1}{\lambda}$ 4555, a line may be seen even beyond this about $\frac{1}{\lambda}$ 4668?		

It is worthy of remark, as showing the purity of these solutions, that the silver nitrate has retained absolute freedom from deposit or any sign of coloration after being exposed to light for two years. It is also quite neutral to litmus.

*3rd Series.*—In this series of observations, advantage was taken of the fact that the nitrates as a rule show their most characteristic absorption spectra between the dilutions of 1/20th to 1/100th of a normal solution.

This is to be observed by examining the *1st* and *2nd Series*. The meaning to be attached to the expression 1/20th normal is that an equivalent weight of a salt in grams is contained in the volume of twenty litres of water, and so on.

*3rd Series.—Nitric Acid.*

Normal solution; 63 grams per litre. Column of liquid, 200 mm.

Dilution.	Spectrum continuous to $\frac{1}{\lambda}$ .		
1/20	3069.	<b>Absorption band.</b>	Ray just visible at 3836.
1/30	3069.	$\frac{1}{\lambda}$ .	Rays transmitted.
1/40	3084.	<b>3084 to 3652.</b>	3652 to 3894.
1/50	3084—3156.	<b>3156 to 3585.</b>	3585 to 3894.
1/60	3084—3156.	<b>3156 to 3545.</b>	3545 to 3940.
1/70	3156.	<b>3156 to 3497.</b>	3497 to 3940.
1/80	3156.	<b>3156 to 3497.</b>	3497 to 3940.
1/90	3156.	Lines exceedingly feeble are transmitted here.	3504 to 3940.
			These lines are not of normal intensity.

*3rd Series.—Lithium Nitrate, LiNO<sub>3</sub>.*

Normal solution ; 69 grams per litre or 13·8 grams in 200 c.c. Column of liquid, 200 mm.

Dilution.	Spectrum continuous to $\frac{1}{\lambda}$ .	Absorption band. $\frac{1}{\lambda}$ .	Rays transmitted. $\frac{1}{\lambda}$ .
1/20	3069.	3069 to 3766.	3766 to 3900.
1/30	3076.	3076 to 3579.	3579 to 3900.
1/40	3149.	3149 to 3495.	3495 to 3900.
1/50	3149.	3149 to 3495.	3495 to 3940.
1/60	3149.	3149 to 3495.	3495 to 3940.
		Rays very feebly transmitted.	
1/70	3149.	The same.	The same.
		Absorption band. $\frac{1}{\lambda}$ .	
1/80	3267. Very feeble.	3267 to 3459.	3459 to 3940.
1/90	The same.	Absorption band. Still strong, but there are some rays feebly visible in it, which indicates that it is about to be weakened.	3940.

It was found subsequently that this salt contained water in the proportion indicated by three molecules of water to four of lithium nitrate. This requires 82·5 grams instead of 69 grams per litre.

*3rd Series.—Silver Nitrate.*

Normal solution. Column of liquid, 200 mm.

Dilution.	Spectrum continuous to $\frac{1}{\lambda}$ .	Absorption band. $\frac{1}{\lambda}$ .	Rays transmitted. $\frac{1}{\lambda}$ .
1/20	3004—3069.		Rays just visible at 3836.
1/30	3069.	3069 to 3579.	3579 to 3900.
1/40	3069.	3143 to 3579.	3579 to 3900.
1/50	3148.	3149 to 3495.	3495 to 3900.
1/60	3149.	3149 to 3495.	3495 to 3900.
1/70	3149.	3149 to 3495.	3495 to 3900.
1/80	3149.	3149 to 3495, but rays very feebly transmitted from 3267 to 3300.	3495 to 3900.
1/90	3149.	Rays very feebly transmitted.	3495 to 3900.



*4th Series.*—A fourth series was taken in which normal solutions were not diluted, but examined in columns of different lengths, commencing with 200 mm. and decreasing thus: 100 mm., 50 mm., 40 mm., 30 mm., 25 mm., 15 mm., 10 mm., 5 mm., 4 mm., 3 mm., 2 mm. As through 200 mm. the absorption effect is caused by one gram-molecular weight of the salt, in 2 mm. it is the effect of 1/100th of this weight. This remark is equally applicable to the dyad metals to which the term 'normal' must be applied in the usual sense of  $\text{NO}_3/1000$  employed in volumetric analysis.

Comparison of differences in length of column of liquid of normal strength with the corresponding dilutions:

200 mm.	Normal	15 mm.	3/40ths Normal
100	1/2 "	10	2/40ths "
50	1/4th "	5	1/40th "
40	1/5th "	4	1/50th "
30	3/20ths "	3	3/200ths "
25	1/8th "	2	1/100th "
20	1/10th "	1	1/200th "

*Lithium nitrate.* 69 grams of salt per litre or 13.8 grams in 200 c.c. of solution. This was intended to be a normal solution, but after it had been made up, I determined the quantity of water in the salt and found it to be in the proportion of  $3\text{H}_2\text{O}$  to  $4\text{LiNO}_3$ , but it is not to be supposed that this was in the nature of a crystalline hydrate, the salt being somewhat hygroscopic. The solution of lithium nitrate, instead of being normal, was only 5/6th normal, as 83 parts should have been dissolved instead of 69.

*4th Series.—Lithium Nitrate.* From 200 mm. to 2 mm.

Thickness.	Spectrum continuous to $1/\lambda$ .	Absorption band. $1/\lambda$ .	Rays transmitted.
mm.			
200	2884.		
100	2938.		
50	2938 feebly to 3000.		
40	3000.		
30	3000.		
25	3000 feebly to 3062.		
15	3000 feebly to 3076		
10	3076.	3076 to 3766.	3766 to 3900.
5	3076 feebly to 3149.	3149 to 3766.	3766 to 3900.
4	3149.	3149 to 3488.	3488 to 3940.
		Lines very feebly seen about 3267 and 3808.	
3	3149.	The same.	3488 to 3940.
2	3149. Rays weak, but continuous to		3940.

*4th Series.—Sodium Nitrate, NaNO<sub>3</sub>.*

Normal solution ; 85 grams per litre, or 17 grams per 200 c.c.

Thickness.	Spectrum continuous to		
mm.	<sup>1</sup> /λ.		
200	2938.		
100	2990.		
50	2990.		
30	3004.		
20	3004—3069 very feeble.		
15	3004—3069 feeble.	<b>Absorption band.</b>	<b>Rays transmitted</b>
		<sup>1</sup> /λ.	very feebly.
10	3069.	<b>3069 to 3766.</b>	<b>3766 to 3884.</b>
	Isolated lines.		
5	3069—3155.	<b>3155 to 3579.</b>	<b>3579 to 3900.</b>
4	3069—3155.	<b>3155 to 3535.</b>	<b>3535 to 3900.</b>
3	3069—3155.	<b>3155 to 3504.</b>	<b>3504 to 3900.</b>
2	3069—3155	<b>3155 to 3440.</b>	<b>3440 to 3940.</b>
		<b>Rays here transmitted</b>	
		very feebly.	
		<b>3274 to 3308.</b>	

*4th Series.—Potassium Nitrate, KNO<sub>3</sub>.*

Normal solution.

Thickness.	Spectrum continuous to		
mm.	<sup>1</sup> /λ.		
200	2884.		
100	2940.		
50	2940—2983.		
40	2983—3004.		
30	3004.		
20	3047—3069.	<b>Absorption band.</b>	<b>Line very faint at</b>
15	3047—3069.	<sup>1</sup> /λ.	3836.
10	3069.	<b>3069 to 3760.</b>	3836.
			3760 to 3900 very feeble.
5	3076—3155.	<b>3155 to 3579.</b>	<b>3579 to 3900.</b>
4	3155.	<b>3155 to 3504.</b>	<b>3504 to 3940.</b>
3	3190.	<b>3190 to 3459.</b>	<b>3459 to 3979.</b>
		<b>Rays about 3274 and</b>	
		<b>3375 feebly trans-</b>	
		<b>mitted.</b>	
2	3190.	<b>Rays transmitted from 3267 to 3979, but</b>	
		<b>very imperfectly between 3341 and 3459.</b>	

*4th Series.—Thallium Nitrate.*

Owing to the sparing solubility of this salt, the solution was made 1/4th normal. 200 mm. to 2 mm.

Thickness.	Spectrum continuous to		
mm.	$\frac{1}{\lambda}$ .		
200	2946.		
100	3004.		
50	3004 to 3069 feeble.		
40	3069.	<b>Absorption band.</b>	Very feebly transmitted.
		$\frac{1}{\lambda}$ .	
30	3069.	3069 to 3652.	3652 to 3836.
25	3069 feebly to 3155.	3155 to 3535.	3535 to 3894.
15	3069 „ 3155.	3155 to 3535.	3535 to 3894.
10	3155.	3155 to 3440.	3440 to 3940.
		Rays very feebly transmitted about 3267 and 3375.	
5, 4, 3, and 2	Rays continuous and strong to 3267 and feeble from 3267 to 3979.		

There is a deceptive appearance when curves are drawn from spectra taken only at the above points, so that, for instance, thallium nitrate appears practically the same as potassium nitrate when allowance is made for differences in the strengths of the respective solutions. Compare the curves of the 1st *Series* and it will be seen that there is a great difference between them.

*4th Series.—Magnesium Nitrate, Mg(NO<sub>3</sub>)<sub>2</sub>, 6H<sub>2</sub>O.*

Normal solution ; 256.4 grams per litre, or 51.3 grams per 200 c.c.

The spectra of the dyad metals are not strictly comparable with those of the monad group.

Thickness.	Spectrum continuous to		
mm.	$\frac{1}{\lambda}$ .		
200	2798.		
100	2884.		
50	2938.		
40	2938.		
	Isolated line.		
35	2938—2990.		
30	2990—3004.		
20	2990—3004.		
15	2990—3004.		
10	3004—3069 very faint.		An isolated line very faint.
5	3069.	<b>Absorption band.</b>	3842.
		$\frac{1}{\lambda}$ .	
4	3069.	3069 to 3772.	3772 to 3900.
3	3069—3149	3149 to 3652.	3652 to 3900.
	very feeble.		
2	3069—3149	3149 to 3504.	3504 to 3940.
	very feeble.		

*4th Series.—Calcium Nitrate,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Ordway).*

Normal solution ; 47.2 grams per 200 c.c.

Thickness.	Spectrum continuous to		
mm.	$1/\lambda$ .		
200	2938.		
100	2938.		
50	2938.		
40	3004.		
30	3004.		
25	3004.		
20	3069.	Absorption band. Line indicated faintly.	
15	3069.	Absorption band. 3842.	
10	3069.	$1/\lambda$ .	3842 very feeble.
5	3069—3149 very faint.	3149 to 3772	3772 to 3905 feebly visible.
4	3069—3149 very faint.	3149 to 3660.	3660 to 3905 feeble.
3	3076—3149.	3140 to 3504.	3504 to 3916. Rays feebly transmitted.

*4th Series.—Zinc Nitrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .*

Normal solution ; 297 grams per litre, or 59.46 grams per 200 c.c.

Thickness.	Spectrum continuous to		
mm.	$1/\lambda$ .		
200	2884.		
100	2884.		
50	2938.		
40	2938—2975.		
30	2975.		
20	2975—3002.		
15	3002—3076.		
10	3076.	Absorption band.	
5	3076.	$1/\lambda$ .	Rays transmitted.
4	3076.	3076 to 3646.	3646 to 3894 very faintly.
3	3076—3155.	3155 to 3646.	3646 to 3894 feeble.
2	3155—3328.	3328 to 3426.	3426 to 3940 feeble.

*4th Series.—Barium Nitrate.*

This salt being sparingly soluble, a solution 1/4th normal was used ;  
65.25 grams per litre ; 200 mm. to 2 mm.

Thickness.	Spectrum continuous to		
mm.	$\frac{1}{\lambda}$ .		
200	2988.		
100	2988 to 3004 feeble.		
50	3004 to 3047 feeble.		
40	3004 to 3047 feeble.	Absorption band.	
		$\frac{1}{\lambda}$ .	Rays transmitted.
80	3047.	3047 to 3772.	3772 to 3905.
25	3047.	3047 to 3772.	3772 to 3905.
15	3047 to 3155 very faint.	3155 to 3552.	3552 to 3905.
10	3047 to 3155 feeble.	3155 to 3535.	3535 to 3940.
5	3204.	3204 to 3535.	3535 to 3935.
		Rays fully transmitted here. Partial absorption.	Strong and continuous.
4	3204.	Absorption band still visible although rays fully transmitted.	3471 to 3935.
3	Continuous spectrum to 3935, but enfeebled between 3204 and 3471.		
2	Absorption between 3204 and 3471 almost invisible.		

*4th Series.—Lead Nitrate.*

A sparingly soluble salt. The solution was made seminormal ; 165.45 grams per litre ; 200 mm. to 2 mm.

Thickness.	Spectrum continuous to		
mm.	$\frac{1}{\lambda}$ .		
200	2884.		
100	2884 feebly to 2938.		
50	2938 feebly to 2982.		
40	2990 feebly to 3007.		
30	3007.		
25	3007 to 3047 feebly.		
20	3067 to 3062 feebly.	Absorption band.	
15	3062.	$\frac{1}{\lambda}$ .	Rays transmitted.
10	3062 to 3148 feebly.	3148 to 3760.	3760 to 3836.
5	3062 to 3148 feebly.	3148 to 3760.	3760 to 3836 stronger.
4	3148 to 3272 feebly.	3274 to 3535.	3535 to 3894.

There is a slight difference in the curves drawn from the measurements of the magnesium, calcium, and zinc nitrates when normal solutions of each are examined in columns of 200 mm. long and shorter columns down to 20 mm., also in smaller thicknesses varying between 15 mm. and 2 mm.

The variation is in the extent of the continuous rays transmitted in the first instance, and in the form of the curve in the second. The barium and lead nitrates present considerable differences with respect to absorption of the rays in small thicknesses. These salts are, however, less soluble than the former, and the results, in consequence, are not quite strictly comparable without corrections for the barium nitrate and lead nitrate, their solutions being one-quarter normal and semi-normal respectively.

Gram-molecular weights of the following nitrates contained in 1000 c.c., show a complete absorption of all rays beyond the wavelengths indicated, when a column 200 mm. in length is photographed.

	$\frac{1}{\lambda}$	$\lambda$		$\frac{1}{\lambda}$	$\lambda$
H.....	2884	346	Mg.....	2798	357
Li.....	2884	346	Ca.....	2938	340
Na .....	3938	340	Zn .....	2884	346
K.....	2884	346	Tl $\frac{1}{4}$ <sup>th</sup> .....	2946	340
Ag .....	2815	355	Ba $\frac{1}{4}$ <sup>th</sup> .....	2938	340
			Pb $\frac{1}{2}$ .....	2884	346
			Er .....	2905	343
			Th $\frac{1}{100}$ <sup>th</sup>	2883	346

*Series 5.*—Comparison of the spectra of nitric acid, potassium nitrate, and silver nitrate, when normal solutions are examined in cells of different thicknesses, and when these solutions are diluted in a corresponding ratio and contained in a tube of 200 mm. in length. Thus 10 mm. of a normal solution were compared with 200 mm. of a solution  $\frac{1}{20}$ th normal, and 4 mm. of a normal solution with 200 mm. of one  $\frac{1}{50}$ th normal. It may be remarked here that measurements of spectra cannot be made with such accuracy through 200 mm. as through 10 mm. or any smaller thickness, the boundary of the absorption bands being not so sharp, hence some difference in the reading may be anticipated. The refraction of the length of the column of liquid tends towards a diffusion of the absorbed rays.

*5th Series.—Nitric Acid.*

	Rays continuous to	Absorption band.	Rays transmitted.
mm.	$\frac{1}{\lambda}$	$\frac{1}{\lambda}$ $\frac{1}{\lambda}$	$\frac{1}{\lambda}$ $\frac{1}{\lambda}$
200—1/20th	3084	3084 to 3772	3772—3784—3905
10—normal	The same feeble	The same	The same
200—1/50th	3084—3155	3155 to 3504	3504 to 3940
4—normal	The same	The same	The same

*Potassium Nitrate.*

200—1/20th	$\frac{1}{\lambda}$ 3069	3069 to 3766	3766, 3782, 3836
10—normal	The same feeble	The same	The same
200—1/50th	3069—3155	3155 to 3510	3510, 3540, 3905
4—normal	The same	The same	The same

*Silver Nitrate.*

10—normal	3004	—	none
5—normal	3069	3069 to 3585	3585, 3652, 3706
4—normal	3069	3069 to 3540	the last barely visible
			3504, 3585, 3652
200—1/20th	3004—3069 feeble	—	none
200—1/40th	3069	3069 to 3579	3579 to 3900
200—1/50th	3148	3148 to 3579	3579 to 3900

From another solution of silver nitrate and another series of photographs :

10—normal	3002	—	none
4—normal	3067	3067 to 3531	3531 to 3638
200—1/20th	3067	—	—
200—1/50th	3067—3150 feeble	3150 to 3531	3531 to 3888

It will be observed that in nitric acid and potassium nitrate, 200 mm. of 1/20th normal solution yields the same spectrum as 10 mm. of a normal solution ; and 200 mm., 1/50th normal, the same as 4 mm. of the normal solution. ut with silver nitrate there is a considerable difference in this respect, inasmuch as the more dilute solutions transmit rays more freely through thicknesses 20 and 50 times as great as that of the solution which is of normal strength, although no less than the same quantity of nitrate is contained in each corresponding solution.

This difference I believe to be due to the action of light, although I do not propose at this stage of the investigation to formulate any views of the actual change in the constitution of the solution, whether due to ionisation or otherwise, but there is reason to believe that the action of radiant energy on dilute solutions is of more frequent occurrence than is usually admitted or taken into account; in other words, there are several other salts which are affected besides those to which such action is usually admitted to be a cause of change in constitution. I will merely mention three, namely, cobalt, nickel, and manganese; to these, I think, may also be added lithium. In the three former, we must not lose sight of the possible effect of atmospheric oxygen, although whatever the effect of oxygen may be, it is light which brings about the change. It is not only on the surface, but within the liquid and upon that side of the containing vessel which is exposed to the light that the action is most vigorous. This fact was observed in nickel bromide, independently of any observations of mine, by Mr. J. A. Cunningham, B.A., who was assisting me at the time with some work on the properties of solutions (*Sci. Trans. Roy. Dubl. Soc.*, 1900, [ii], 7, 253).

It is worthy of note, as tending to dispel all doubts on the subject of the purity of the silver nitrate solutions, that they were perfectly neutral, and that they have been kept for more than 2 years in white glass bottles freely exposed to the light of day without the slightest change in their appearance. This is a proof that no organic matter or any impurity has affected them.

The absorptive power of the thorium salt is very astonishing. On the first plate that was exposed there was little of a spectrum to be seen. The solution was then diluted 100 times, and through 200 mm. a continuous spectrum was transmitted as far as wave-length 346.

These measurements serve to explain what has been recorded by Liveing (*Trans. Camb. Phil. Soc.*, 1900, 18, 298), namely, that strong solutions of the nitrates have a general absorption of the more refrangible rays, and in this respect these salts differ from the chloride and acetate of didymium and from the chloride of erbium.

At a future date, an account will be given of some solutions which, owing to their mode of preparation, may be deemed to be more strictly comparable with each other, and an opportunity may then occur of discussing the whole of the results.

*Notes.*—Since the above was written, G. P. Drossbach (*Ber.*, 1902, 35, 91), working with 10 per cent. solutions of colourless metallic nitrates and a thickness of 20 mm. of liquid, finds that there is a general absorption of the rays beyond  $\lambda$  340. Absorption bands become visible when the solutions are diluted.

I have purposely excluded from the present communication an

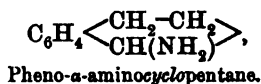
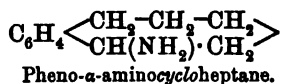


account which had been prepared of the finely-marked absorption bands exhibited in the ultra-violet region by nickel, cobalt, and uranium, in the form of bromides, chlorides, and acetates. The bands are characteristic of the metallic elements, and they lie in a region of rays less refrangible than that of the bands of the nitrates. In some cases, one band is affected by the other, so that the question which is in course of investigation would become complicated.

LXI.—*The Resolution of Pheno- $\alpha$ -aminocycloheptane into its Optical Isomerides. Tartrates of Pheno- $\alpha$ -aminocycloheptane and of Hydrindamine.*

By FREDERIC STANLEY KIPPING and ALBERT EDWARD HUNTER.

PHENO- $\alpha$ -AMINOCYCLOHEPTANE (Kipping and Hunter, Trans., 1901, 79, 602) and pheno- $\alpha$ -aminocyclopentane ( $\alpha$ -hydrindamine), being very similar in constitution, especially with regard to the nature and position in the molecule of the asymmetric carbon group, as shown in the following formulæ,



it seemed possible that the two bases would behave in a similar manner towards a given optically active acid; if this actually proved to be the case, the study of the compounds of pheno- $\alpha$ -aminocycloheptane might throw some light on the nature of those hydrindamine salts which have recently been investigated (Kipping, Trans., 1900, 77, 861; 1901, 79, 430) and appear to be altogether abnormal.

The experiments which have so far been made with the cycloheptane derivative have shown, however, that the two bases behave quite differently; whereas *dl*-hydrindamine hydrogen tartrate is not changed by fractional crystallisation from water, the corresponding compound of *dl*-pheno- $\alpha$ -aminocycloheptane with *d*-tartaric acid is readily resolved into the salts of its enantiomorphously related components.

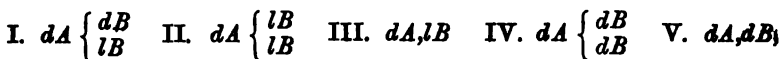
Of these two salts, the more sparingly soluble is that of the *l*-base, which is thus easily isolated; it is almost optically inactive, owing to the molecular rotation of the base being approximately equal to that of the acid, but of opposite sign.

The active base does not show the least tendency to undergo racemisation, and when liberated from its salts or when submitted to

distillation in steam, its optical properties seem to remain absolutely unchanged; further, when treated with benzoyl chloride and sodium hydroxide, it yields an optically active benzoyl derivative, and although the sign of rotation is changed, there is no evidence of even partial racemisation having occurred.

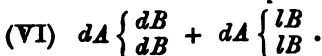
These observations might be quoted in support of the view that the existence of the hydrindamine salts already referred to cannot be explained by assuming that the optically active hydrindamines immediately undergo complete racemisation when liberated from their salts (Trans., 1900, 77, 878, 909); but considering that in the case of other bases, almost as closely related to pheno-*α*-aminocycloheptane in constitution, as, for example, in that of tetrahydro-*β*-naphthylamine (Pope and Harvey, Trans., 1901, 79, 74), partial racemisation occurs when the base is set free from its salts and when it is benzoylated by the Schotten-Baumann method, it would seem that arguments based on analogy have little, if any, value as regards such reactions. It would follow, therefore, that even if racemisation of amino-compounds, in which the amino-group is directly united with the asymmetric carbon atom, is due to tautomeric changes,  $>\text{CH}\cdot\text{NH}_2 \rightleftharpoons >\text{C}\cdot\text{NH}_2$ , as previously suggested, such changes are not necessarily intermediate steps in the formation of salts or in the production of alkyl derivatives.

The relationship between the various salts which have been obtained from *dl*-pheno-*α*-aminocycloheptane and *d*-tartaric acid is not without interest, and of the five (or six) compounds which might be prepared, namely,



all have been isolated and studied.

The first of these compounds, a normal salt, is deposited from neutral and also from acid solutions; it may be regarded as a partially compensated compound, but may possibly be more complex in character and consist of a partially racemic compound of the two salts,



The normal salt of the *l*-base (II) cannot be obtained directly by crystallising solutions of the *dl*-base in aqueous tartaric acid, but was prepared from the pure *l*-base; it is more readily soluble in water than the normal salt (I) of the *dl*-base, and also more readily soluble than the hydrogen salt (III).

The hydrogen salt of the *l*-base (III) is obtained by crystallising a solution of the *dl*-base in a large excess of aqueous *d*-tartaric acid, and is consequently more sparingly soluble than the corresponding salt of the *d*-base (V); it contains 3 mols.  $\text{H}_2\text{O}$ . The normal salt of the

*d*-base (IV) can be isolated from the mother liquors obtained in the crystallisation of the preceding compound; it is anhydrous. The hydrogen salt of the *d*-base (V) was obtained by crystallising the normal salt from aqueous tartaric acid.

The tartrates of *dl*-hydrindamine behave differently from the corresponding salts of the *cycloheptane* base. The hydrogen tartrate is easily obtained in crystals from a solution of the base (1 mol.) in aqueous *d*-tartaric acid (1 mol.); it is readily soluble in water, and is unchanged on repeated fractional crystallisation. The normal tartrate is still more readily soluble, and does not yield salts of enantiomorphously related bases when fractionally crystallised.

The bromocamphorsulphonates of pheno- $\alpha$ -aminocycloheptane and of hydrindamine, like the tartrates, fail to show the similarity in properties which might have been expected; whereas the salt of *dl*-hydrindamine crystallises very readily and can be resolved into unequal quantities of the isomerides already described (Kipping, *loc. cit.*); that of the *dl*-cycloheptane base is usually deposited as an oil which solidifies very slowly and does not lend itself to fractional crystallisation. The bromocamphorsulphonate of the *l*-base, on the other hand, crystallises with great facility even at about 100°, so that the opposite behaviour of the *dl*-salt is obviously due to the fact that it is a mixture.

The examples afforded by the above salts may be employed to give precision to the term 'partial racemism' or 'partially racemic' which, first used by E. Fischer (compare Ladenburg, *Ber.*, 1898, 31, 938), has come to be employed rather in a wide sense to denote salts of a *d*- or *l*-acid with a *dl*-base, or of a *d*- or *l*-base with a *dl*-acid, which may be very different in character.

According to Ladenburg (*loc. cit.*), a partially racemic compound is "eine Verbindung zweier Körper, die nur theilweise Spiegelbilder sind, so dass also durch die Verbindung nur eine theilweise Aufhebung der optischen Activität stattfindet und der racemische Körper noch optische Activität besitzt," and he applies this definition more particularly to the salt of *dl*-methylglutaric acid with quinine and to the salt of *dl*-tartaric acid with strychnine (*Ber.*, 1898, 31, 1969); these salts, however, he seems to regard as derivatives of racemic acids, for he says further that the quinine salt "kein Gemisch der Salze von *d*- und *l*-Säure, sondern ein einheitliches Salz ist, also nur das Salz der racemischen Säure sein kann," and he also represents the strychnine salt by the formula  $rC_4H_6O_6, 2C_{21}H_{22}O_2N_2, 6\frac{1}{2}H_2O$ .

Now it is rather difficult to understand Ladenburg's point of view in this matter, since a racemic acid is merely a crystalline combination of the *d*- and *l*-isomerides, and has no existence except in such a form; when combined with a base, a racemic acid ceases to exist, and there are

formed salts of the *d*- and *l*-acids, which may behave in various ways.

Considering this point more generally, an externally compensated dibasic acid and an optically active mon-acid base may unite in solution to form two normal salts, namely,  $dA \left\{ \begin{smallmatrix} dB \\ dB \end{smallmatrix} \right.$  and  $lA \left\{ \begin{smallmatrix} dB \\ dB \end{smallmatrix} \right.$  analogous compounds being produced, namely,  $dA, dB$ , and  $lA, dB$ , if the acid be monobasic or if, being dibasic, the hydrogen salts are formed.

The two salts thus produced (1) may be different in physical properties and may be separable by fractional crystallisation as is frequently, if not usually, the case; (2) they may unite crystallographically when deposited from solution, giving a substance differing in crystalline form and in other physical properties from one or from both its components; (3) they may possibly be deposited from solution side by side in equal quantities forming a mere mixture; (4) they may possibly form a crystalline intercalation, somewhat similar to a pseudoracemic substance (Kipping and Pope, *Trans.*, 1897, '71, 989) as regards its crystallographic relationship to its components.

An optically active dibasic acid and an externally compensated base may unite in solution to form three normal salts, namely, (a)  $dA \left\{ \begin{smallmatrix} dB \\ lB \end{smallmatrix} \right.$  (b)  $dA \left\{ \begin{smallmatrix} dB \\ dB \end{smallmatrix} \right.$  and (c)  $dA \left\{ \begin{smallmatrix} lB \\ lB \end{smallmatrix} \right.$ ; on crystallising, the salt containing both bases in one molecule may alone be deposited as a definite compound, but if not, the mixture of the two salts (b) and (c) may possibly behave in any one of the four ways already enumerated.

Corresponding possibilities are of course to be expected when, in any of the above cases, the dibasic acid and mon-acid base are exchanged for a di-acid base and a monobasic acid.

Now in all the above cases, except in that in which a separation occurs on fractional crystallisation and in that in which only one kind of molecule (a) is produced, the salt conforms to Ladenburg's definition unless the meaning of 'Verbindung' be interpreted as a crystallographic union, the result of which is to give a product differing from at least one of its components in crystalline form, and consequently in other properties; if this limitation be not made, the term 'partially racemic' would include a number of salts of different types in much the same way as did at one time the term racemic (Kipping and Pope, *loc. cit.*)

Before classing a salt as a partially racemic compound, it is necessary therefore to compare its behaviour with that of its component salts in much the same way as is necessary in characterising a racemic compound; according to Roozeboom (*Zeit. physikal. Chem.*, 28, 1899, 494), the method based on solubility determinations with mixtures of equal

and of unequal quantities of the two component salts may be made use of, but no experiments of this kind seem to have been made.

Returning to the tartrates described above, it would seem that the partially racemic hydrogen salt of pheno- $\alpha$ -aminocycloheptane does not exist, as the mixture of the two components  $dA, dB$ ,  $dA, lB$ , shows the behaviour noted under (1). The normal tartrate of the  $dl$ -base, which differs crystallographically from the normal salt of the  $l$ -base, may be either a partially racemic salt or consist of identical molecules  $dA \begin{Bmatrix} dB \\ lB \end{Bmatrix}$ ; to class a compound of the latter type as partially racemic would be obviously incorrect, and opposed to the whole meaning of the word racemic as now used; as, therefore, there are no means of distinguishing between the two possibilities, the salt may, for the present, be classed as a partially compensated substance.

The existence of partially externally compensated salts which are mere mixtures of equal quantities of their components, and which, nevertheless, cannot be resolved by fractional crystallisation, seems to be doubtful, although, possibly,  $dl$ -hydrindamine  $d$ -mandelate is an example of such a substance (Kipping and Hall, *Trans.*, 1901, 79, 443).

#### EXPERIMENTAL.

##### *dl*-Pheno- $\alpha$ -aminocycloheptane Tartrate.

When  $dl$ -pheno- $\alpha$ -aminocycloheptane, partly dissolved and partly suspended in water, as obtained by distilling in steam, is neutralised with  $d$ -tartaric acid and the solution then concentrated and allowed to cool, a salt separates in highly lustrous needles or prisms, and further quantities of the same compound are obtained on again concentrating the mother liquors.

This salt has a neutral reaction to litmus, and is the normal salt of the  $dl$ -base; it has the composition  $C_4H_6O_6 \cdot 2C_{11}H_{15}N$ . It is only sparingly soluble in cold water, but dissolves fairly easily on boiling; it melts and decomposes at about  $235^\circ$ , but the rate of heating influences the result very considerably, temperatures ranging from  $230^\circ$  to  $240^\circ$  being observed, according as the salt is slowly or rapidly heated.

The specific rotation of the  $dl$ -salt was determined in aqueous solution with the following result:

0.25 gram of air-dried salt dissolved in water and the solution diluted to 25 c.c. gave in a 200 mm. tube  $\alpha + 0.26^\circ$ , whence  $[\alpha]_D 13^\circ$ .

The molecular rotation of the salt is therefore  $[M]_D + 60^\circ$ , a value which agrees fairly well with that calculated from the specific

rotations of the normal metallic tartrates, namely,  $[\text{M}]_{\text{D}} + 67^{\circ}$  (compare Landolt, *Das optische Drehungsvermögen*).

Fractional crystallisation of this normal tartrate from water does not seem to resolve it into salts of the *d*- and *l*-bases, and the salt may be regarded as a partially compensated compound having the composition  $dA \left\{ \frac{dB}{lB} \right.$  or  $dA \left\{ \frac{dB}{dB} + dA \left\{ \frac{lB}{lB} \right.$ ; the attempts to resolve it into different fractions by crystallisation were not carried beyond two or three operations, owing to the occurrence of hydrolytic dissociation and consequent loss of base.

#### *Salts of 1-Pheno- $\alpha$ -aminocycloheptane.*

*1-Pheno- $\alpha$ -aminocycloheptane Hydrogen Tartrate.*—The mother liquors remaining after the separation of several crops of crystals of the normal salt just described give, finally, deposits consisting of very slender needles, which form felted masses quite unlike the prisms of the normal salt; these very slender crystals consist of the hydrogen tartrate, as was proved by titrating a dried and weighed sample with sodium hydroxide solution. The presence of this salt is not due to excess of tartaric acid having been added, originally, but to the fact that the normal salt is partially dissociated hydrolytically in aqueous solution, and on boiling or evaporating on the water-bath the base volatilises with the steam.

In order to prepare the hydrogen salt in larger quantities, the normal salt was mixed with one molecular proportion of *d*-tartaric acid and the mixture dissolved in a considerable quantity of hot water; on cooling, however, the normal salt was deposited unchanged and the mother liquors gave only small quantities of the hydrogen salt together with the tartaric acid which had been added, and most of which had remained uncombined. This rather unusual behaviour is doubtless due to the fact that in solutions containing the hydrogen salts of the *d*- and *l*-bases, the normal partially compensated compound is more sparingly soluble than either of the hydrogen tartrates, and on crystallising a change occurs which may be presented as follows,  $dA, dB + dA, lB = dA \left\{ \frac{dB}{lB} + dA \right.$ .

On adding a considerable quantity of *d*-tartaric acid to a solution saturated with the normal *dl*-salt and containing a few crystals of the latter in suspension, the crystals slowly dissolve, but on concentrating the solution and allowing it to cool, the normal salt is again deposited in the first fractions, apparently in a pure condition; if, however, the proportion of *d*-tartaric acid present in solution be increased, the first fractions consist of a mixture of the normal *dl*-salt and of the hydrogen

salt, until at last, by using a very large excess of the acid, crystals of the hydrogen tartrate are deposited almost, but not quite, free from those of the normal salt.

The pheno- $\alpha$ -aminocycloheptane hydrogen tartrate which is thus obtained is the salt of the *l*-base; after one recrystallisation from water, it was obtained in needles melting at about  $175^\circ$  and having a specific rotation of about  $[\alpha]_D + 4^\circ$ . On repeated crystallisation, it seems to be completely separated from any normal salt and from the hydrogen salt of the *d*-base, and is thus obtained in lustrous needles or prisms very similar in appearance to the crystals of the normal *dl*-salt. It melts and decomposes at  $181$ — $182^\circ$ , the rate of heating having very little effect on the melting point.

Unlike the normal salt, it contains water of crystallisation :

0.1936 lost 0.0282  $H_2O$  at  $100^\circ$ .  $H_2O = 14.5$ .

0.2711 „ 0.0370  $H_2O$  over sulphuric acid and 0.0015 at  $100^\circ$ .  $H_2O = 14.2$ .

$C_4H_6O_6, C_{11}H_{15}N, 3H_2O$  requires  $H_2O = 14.8$  per cent.

It seems to be rather more readily soluble in cold water than the normal partially compensated salt, but it is only sparingly soluble in this liquid and also in ethyl alcohol; it crystallises from water unchanged even in absence of tartaric acid.

As this salt is formed by the combination of a dextrorotatory acid with a levorotatory base, and as the two compounds have approximately the same molecular rotations, but of opposite signs, solutions of the salt are almost optically inactive.

Two different samples were examined with the following results :

0.4560 gram of dehydrated salt dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha - 0.03^\circ$ ;  $[\alpha]_D - 0.8^\circ$ .

0.4974 gram of dehydrated salt under the same conditions gave  $\alpha - 0.10^\circ$ ;  $[\alpha]_D - 2.5^\circ$ .

The readings in these experiments being so small, the agreement may be considered as fairly satisfactory, and the molecular rotation, calculated from the mean value, may be taken as  $[M]_D = -5^\circ$ .

As the molecular rotation of *d*-tartaric acid in the metallic hydrogen tartrates is  $[M]_D + 42^\circ$ , that of the levorotatory base would be  $[\alpha]_D - 47^\circ$ , a value which agrees very well with that obtained from observations made with its hydrochloride.

*l*-Pheno- $\alpha$ -aminocycloheptane Tartrate.—On adding an alcoholic solution of *d*-tartaric acid to an ethereal solution of *l*-pheno- $\alpha$ -aminocycloheptane, keeping the base in excess, the normal tartrate is deposited in crystals which melt fairly sharply at  $215$ — $217^\circ$ , effervescing and turning slightly brown.

The salt thus obtained was quickly dissolved in hot water and the solution rendered alkaline with the *l*-base; from this solution it was deposited in flat, transparent, triangular plates, very different in appearance from the crystals of the partially compensated normal salt, and apparently anhydrous. It was comparatively easily soluble in hot water, much more so than the hydrogen tartrate, but its solution on boiling gave off half of the base, and on subsequently cooling the hydrogen tartrate (m. p. 181—182°) was deposited. On adding powdered tartaric acid to a cold saturated solution of this normal salt, a heavy precipitate of colourless needles of the hydrogen tartrate was produced.

*l*-Pheno- $\alpha$ -aminocycloheptane Hydrochloride.—This salt was prepared by decomposing the hydrogen tartrate of the *l*-base with sodium hydroxide, distilling in steam, and evaporating the distillate with excess of hydrochloric acid. It separates from water in lustrous, striated needles or prisms and shows no signs of melting when heated at 250°; it is moderately easily soluble in boiling water, sparingly so in cold water, and very sparingly so in ethyl alcohol.

In order to ascertain whether partial or complete racemisation had occurred in the formation of the hydrochloride from the hydrogen tartrate in the above manner, the halogen salt was fractionally crystallised from water and thus separated into two crystalline portions, leaving only a very small quantity in the mother liquors. The two fractions were then dried and examined optically.

*Fraction I.* 0.272 gram dissolved in water, the solution diluted to 25 c.c., and examined in a 200 mm. tube gave  $\alpha$   $-0.52^\circ$ , whence  $[\alpha]_D - 24^\circ$ .

*Fraction II.* 0.264 gram under the same conditions gave  $\alpha$   $-0.50^\circ$ , whence  $[\alpha]_D - 23.7^\circ$ .

It seems from these results that racemisation does not take place either on liberating the active base from its salts or on heating it at 100°, and this conclusion is confirmed by experiments described later.

Taking the mean of the above values, the molecular rotation of the base would be  $[\text{M}]_D - 47^\circ$ , a result which agrees very well with that deduced from the observations made with the hydrogen tartrate.

*Benzoyl-l-pheno- $\alpha$ -aminocycloheptane*,  $\text{C}_{11}\text{H}_{14}\text{N}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ .

This compound was prepared by treating the *l*-base with benzoyl chloride by the Schotten-Baumann method. It was immediately precipitated in crystals, and the crude product, when merely washed with water and dried, melted at 174—175°. It crystallised from alcohol in long, lustrous needles, very similar in appearance to the crystals of the benzoyl derivative of the *dl*-base (Kipping and Hunter, *loc. cit.*); the



two compounds, however, differed in melting point, the derivative of the *l*-base melting at 175—176°, the optically inactive compound at 171—172°, and a mixture of the two from 160—166°.

The benzoyl derivative of the *l*-base is dextrorotatory in methyl alcoholic solution; it is insoluble in cold water, but moderately easily soluble in cold chloroform.

*Picrates of dl- and of l-Pheno- $\alpha$ -aminocycloheptane.*

The picrate of the *dl*-base is obtained as a precipitate, mixed, apparently with a little normal tartrate, on adding a hot aqueous solution of picric acid to a similar solution of the *dl*-tartrate; it crystallises from water in yellow prisms and decomposes at about 205°.

The picrate of the *l*-base, prepared from a solution of the hydrogen tartrate of the *l*-base in a similar manner, crystallises from water in well-defined, yellow prisms and decomposes at about 185°.

The decomposing points of both these picrates depend greatly on the rate of heating, and the compounds are consequently of little use for purposes of identification; they are both moderately easily soluble in methyl alcohol, but only very sparingly so in cold water.

*Salts of d-Pheno- $\alpha$ -aminocycloheptane.*

*d-Pheno- $\alpha$ -aminocycloheptane Tartrate.*—As a rule, it is not very easy to isolate both the bases by crystallising the product of the combination of a *dl*-base with an optically active acid, as, after separating the more sparingly soluble salt of one of the bases, there remains a mixture which usually does not lend itself to further fractional crystallisation. In the case of *dl*-pheno- $\alpha$ -aminocycloheptane, however, owing to the unusual behaviour of its tartrates, salts of both bases can be obtained in a pure condition by one series of crystallisations.

Starting with an aqueous solution of the *dl*-base in a large excess of tartaric acid, the hydrogen tartrate of the *l*-base is first isolated as already described; the mother liquors from this salt give, on evaporation, a deposit which seems to consist of a mixture of both the hydrogen tartrates with free tartaric acid, but on separating this deposit from the remaining aqueous solution of the acid and again dissolving in water, crystals of the normal salt of the *dl*-base are obtained, because the relative quantity of free acid in the solution has been diminished. If, now, the normal, partially compensated salt be separated as far as possible, the mother liquors yield, on evaporation, a mixture of tartaric acid and the normal or hydrogen tartrate of this *d*-base; this normal salt is finally obtained in a pure condition by further fractional crystallisation.

This salt crystallises from water in concentrically grouped needles

or prisms, has a neutral reaction to litmus, and is anhydrous; it melts and decomposes at about  $216\text{--}217^\circ$ , but unless carefully dried its melting point falls to about  $210^\circ$ . It is less readily soluble in water than the hydrogen salt of the *d*-base, and for this reason it is obtained, and can be crystallised, from solutions containing free tartaric acid; in this case, therefore, the behaviour is similar to that of the tartrate of the *dl*-base, and the formation of this normal salt, on crystallising such acid solutions, may be represented as follows:  $2\ dA, dB = dA \left\{ \frac{dB}{dB} + dA \right.$

*d*-Pheno- $\alpha$ -aminocycloheptane Hydrogen Tartrate.—This salt is deposited when excess of tartaric acid is added to a hot solution of the normal salt of the *d*-base and the solution concentrated if necessary; it can also be obtained by boiling a solution of the normal salt, when hydrolytic dissociation occurs and half the base volatilises with the steam. It forms long, slender needles, melts and decomposes at  $205\text{--}206^\circ$ , and seems to be more readily soluble in cold water than the other salts, except, perhaps, the normal tartrate of the *l*-base.

*d*-Pheno- $\alpha$ -aminocycloheptane Hydrochloride.—That the two salts just described are really those of the *d*-base was proved by decomposing the normal salt with sodium hydroxide, distilling in steam, and evaporating the distillate with hydrochloric acid; the hydrochloride thus obtained was identical with that of the *l*-base in ordinary properties, but its solution in water was dextrorotatory.

0.241 gram dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha + 0.42^\circ$ , whence  $[\alpha]_D + 21.8^\circ$ .

Considering the unavoidable experimental errors in dealing with such low specific rotations, this result agrees satisfactorily with that obtained in the case of the corresponding salt of the *l*-base.

### *Tartrates of dl-Hydrindamine.*

The tartrates of *dl*-hydrindamine, as already stated, show little, if any, analogy with those of pheno- $\alpha$ -aminocycloheptane. The hydrogen tartrate is easily obtained by mixing the base with an aqueous solution of one molecular proportion of the acid and then evaporating; it forms masses of small needles or prisms, and is moderately soluble in cold water but only sparingly so in cold alcohol:

1.5285 lost 0.0905  $H_2O$  at  $100^\circ$ .  $H_2O = 5.9$ .

$C_9H_{11}N, C_4H_6O_6, H_2O$  requires  $H_2O = 5.98$  per cent.

The anhydrous salt melts and decomposes at  $168\text{--}169^\circ$ .

The principal points of difference between this salt and the corresponding derivative of pheno- $\alpha$ -aminocycloheptane are, firstly, that this

compound crystallises unchanged in absence of tartaric acid, whereas the mixture of *d*- and *l*-pheno- $\alpha$ -aminocycloheptane salts gives the normal salt of the *dl*-base, and, secondly, that fractional crystallisation fails to resolve the *dl*-hydrindamine salt into its components. A considerable quantity of the hydrogen salt was crystallised from water a great number of times, and the two end fractions were then examined; they were identical in melting point and in outward properties, and on examination in the polarimeter were also found to be identical optically.

0.3955 gram of air-dried salt dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha +0.44^\circ$ , whence  $[\alpha]_D +13.9^\circ$ .

The molecular rotation, calculated for the anhydrous salt, is therefore  $[M]_D +42^\circ$ , and as that of *d*-tartaric acid is  $[M]_D 42^\circ$  in the hydrogen metallic tartrates, it is obvious that the salt contains equal quantities of the *d*- and *l*-bases.

The normal tartrate of *dl*-hydrindamine, prepared by neutralising an aqueous solution of the acid with the base, and allowing this solution to evaporate spontaneously, crystallises in plates and melts at about  $200^\circ$ ; it is much more readily soluble than the hydrogen salt and does not crystallise very well. When its aqueous solution is boiled, hydrindamine volatilises, and subsequently the hydrogen salt is deposited.

#### *l*-Pheno- $\alpha$ -aminocycloheptane Bromocamphorsulphonate.

Since it is with *d*-bromocamphorsulphonic acid that *dl*-hydrindamine forms two well-defined partially externally compensated salts, it seemed possible that the cycloheptane base would yield analogous isomerides. On neutralising an aqueous solution of the acid with *dl*-base and allowing the solution to crystallise spontaneously, the deposits were always of an oily consistency, and only very partially solidified, even in cold weather. Such solutions were therefore not examined further, but a separation of the bases with the aid of tartaric acid having been obtained, the *l*-base was combined with bromocamphorsulphonic acid.

The compound thus obtained crystallised with great facility from aqueous solutions, even on the water-bath, and was deposited in highly lustrous, striated prisms melting at  $216-217^\circ$ ; it was only sparingly soluble in cold water, but readily soluble in alcohol.

The specific rotation was determined by dissolving 0.45 gram in water, diluting the solution to 25 c.c., and examining it in a 200 mm. tube;  $\alpha +1.72^\circ$ , whence  $[\alpha]_D +47.8^\circ$ . The molecular rotation is therefore  $[M]_D +225.6^\circ$ ; taking that of the bromo-acid to be  $+270^\circ$ , the molecular rotation of the base is  $[M]_D -44.4^\circ$ . This result confirms those

previously obtained, and affords additional evidence of the stability of the base as regards racemisation; fractional crystallisation of the bromocamphorsulphonate failed to reveal the presence of any isomeride.

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## LXII.—*Colouring Matter from the Flowers of Delphinium Consolida.*

By ARTHUR GEORGE PERKIN, F.R.S.E., and EDWARD JOHN WILKINSON.

IN a previous communication (Trans., 1898, 73, 267) it was shown that the flowers of *Delphinium zaili* contain as glucosides isorhamnetin, quercetin, and a trace of a third colouring matter. With the desire at the time to study the latter compound more closely, attention was directed to *Delphinium Consolida*, a plant more readily procurable, in the hope that it might contain the same constituents. Experiment showed that the blue flowers contained a moderate quantity of yellow colouring matter which differed in composition from that present in *Delphinium zaili*. This, judging from the melting point of its acetyl derivative, appeared to be a mixture, and as attempts to effect a separation of the substances failed, the subject was laid aside for some time. Recently it was found that the colouring matter was a single substance, and its investigation was therefore proceeded with. *Delphinium Consolida* is a common European plant belonging to the Larkspur family; its name refers to its powers, real or imaginary, of healing or consolidating wounds.

### EXPERIMENTAL.

The flowers themselves were first employed, but subsequently, to economise time and labour, an extract was obtained by purchase from Merck of Darmstadt.

Four hundred grams of this product dissolved in 4½ litres of boiling water were digested at the boiling point with 30 c.c. of sulphuric acid, causing the separation of a light coloured, viscous deposit and a considerable quantity of calcium sulphate. The hot liquid decanted from this was treated with 100 c.c. of sulphuric acid, again boiled for an

hour, and allowed to stand overnight. A dark brown, resinous precipitate containing the colouring matter was thus formed, and this was collected on calico, washed with water, extracted with boiling alcohol, and the extract evaporated to a small bulk. Addition of ether caused the deposition of a tarry product, and the ethereal solution was continuously washed with water until no further impurity separated in this manner. On evaporation, a semi-crystalline mass of the crude colouring matter was obtained, which was collected, well washed with water, and crystallised from dilute alcohol. In this way, 500 grams of the flowers gave 5.13 grams of crude colouring matter or approximately 1 per cent. The product was now converted into its acetyl derivative, and this, when colourless, reconverted into the colouring matter in the usual manner:

0.1128 at 160° gave 0.2614 CO<sub>2</sub> and 0.0319 H<sub>2</sub>O. C = 63.20; H = 3.14.  
 0.1086       "       0.2503 CO<sub>2</sub>   "   0.0345 H<sub>2</sub>O. C = 62.85; H = 3.53.  
 C<sub>15</sub>H<sub>10</sub>O<sub>6</sub> requires C = 62.93; H = 3.49 per cent.

It consisted of pale yellow needles resembling quercetin in appearance, melted at 276—277°, was readily soluble in boiling alcohol and dissolved in alkaline solutions with a pale yellow colour. Alcoholic lead acetate gave an orange precipitate, and alcoholic ferric chloride a greenish-black coloration. It contained no methoxy-group. Addition of potassium acetate to its boiling alcoholic solution caused the separation of minute, orange-yellow, prismatic needles, which were collected with the aid of the pump, washed with alcohol, then with a little water, and finally with alcohol, and dried at 160°:

0.3265 gave 0.0875 K<sub>2</sub>SO<sub>4</sub>. K = 12.01.  
 0.5085   "   0.1345 K<sub>2</sub>SO<sub>4</sub>. K = 12.04.  
 C<sub>15</sub>H<sub>9</sub>O<sub>6</sub>K requires K = 12.03 per cent.

This *monopotassium* salt closely resembles those of quercetin, morin, &c. (Trans., 1899, 75, 433), and is decomposed by water with separation of the free colouring matter.

On adding sulphuric acid to the substance suspended in boiling acetic acid, a *sulphate* was obtained crystallising in orange-red, glistening needles:

0.1159 gave 0.1985 CO<sub>2</sub> and 0.0354 H<sub>2</sub>O. C = 46.70; H = 3.39.  
 C<sub>15</sub>H<sub>10</sub>O<sub>6</sub>.H<sub>2</sub>SO<sub>4</sub> requires C = 46.87; H = 3.12 per cent.

The *hydrochloride* and *hydrobromide* were similarly prepared, but were not analysed, as they suffer decomposition at 100°. The *hydroiodide* was somewhat more stable:

0.1148 gave 0.1863 CO<sub>2</sub> and 0.0310 H<sub>2</sub>O. C = 44.25; H = 3.00.  
 C<sub>15</sub>H<sub>10</sub>O<sub>6</sub>.HI requires C = 43.48; H = 2.65 per cent.

*Action of Bromine.*—To the colouring matter suspended in acetic acid sufficient bromine was added to convert it into a tetrabromo-derivative, rise of temperature being avoided. After standing for 3 days, the product was drained on a porous tile, washed with alcohol, and purified by crystallisation from acetic acid with the aid of animal charcoal:

0.1177 gave 0.1492  $\text{CO}_2$  and 0.0190  $\text{H}_2\text{O}$ .  $\text{C} = 34.57$ ;  $\text{H} = 1.79$ .

0.1525 „ 0.1944  $\text{CO}_2$  „ 0.0185  $\text{H}_2\text{O}$ .  $\text{C} = 34.76$ ;  $\text{H} = 1.34$ .

$\text{C}_{15}\text{H}_7\text{O}_6\text{Br}_4$  requires  $\text{C} = 34.41$ ;  $\text{H} = 1.34$  per cent.

The *tribromo*-compound crystallises in pale yellow needles, sparingly soluble in boiling acetic acid and soluble in alkaline solutions with an orange-yellow coloration. It melts at  $275-277^\circ$ .

The colouring matter has thus the formula  $\text{C}_{15}\text{H}_{10}\text{O}_6$ , and from its reactions is probably a member of the quercetin group.

The *acetyl* derivative, prepared by heating the colouring matter with one part of anhydrous sodium acetate and three of acetic anhydride, crystallised from methyl alcohol in colourless needles. These, when heated, commenced to melt at  $116^\circ$ , became completely fluid at  $120^\circ$ ; on further heating, however, gradual solidification ensued, and the product subsequently melted at  $181-182^\circ$ . When ethyl alcohol was employed, this preliminary liquefaction was not so pronounced, and only a slight sintering at  $120^\circ$  was observed. Investigation showed that no loss in weight occurred during the preliminary fusion, and the resolidified product was not viscous as would be expected if an impurity of low melting point were present. The amount of impurity, if present, must have been infinitesimal, and all attempts to eliminate it were unsuccessful; moreover, there is evidence to show the product was a pure substance:

0.1065 gave 0.2368  $\text{CO}_2$  and 0.0400  $\text{H}_2\text{O}$ .  $\text{C} = 60.64$ ;  $\text{H} = 4.17$ .

$\text{C}_{22}\text{H}_{18}\text{O}_{10}$  requires  $\text{C} = 60.79$ ;  $\text{H} = 3.96$  per cent.

Acetyl determinations in the usual manner gave the following results, indicating that the compound was a *tetraacetyl* derivative:

0.9453 gave 0.6018  $\text{C}_{15}\text{H}_{10}\text{O}_6$ .  $\text{C}_{15}\text{H}_{10}\text{O}_6 = 63.66$ .

4.2595 „ 2.6560  $\text{C}_{15}\text{H}_{10}\text{O}_6$ .  $\text{C}_{15}\text{H}_{10}\text{O}_6 = 62.36$ .

$\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_2\text{H}_5\text{O})_4$  requires  $\text{C}_{15}\text{H}_{10}\text{O}_6 = 63.00$  per cent.

*Fusion with alkali* at  $200-220^\circ$  gave *phloroglucinol* (m. p.  $210^\circ$ ) and a crystalline acid melting at  $208-210^\circ$ . The identity of the latter with *p-hydroxybenzoic acid* was confirmed by analysis:

0.1114 gave 0.2480  $\text{CO}_2$  and 0.0394  $\text{H}_2\text{O}$ .  $\text{C} = 60.71$ ;  $\text{H} = 3.93$ .

$\text{C}_7\text{H}_4\text{O}_3$  requires  $\text{C} = 60.86$ ;  $\text{H} = 4.34$  per cent.

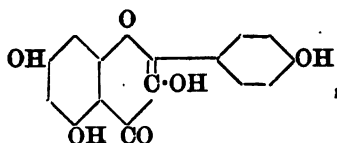
*Dyeing Properties.*—In investigating these, mordanted woollen cloth

was employed, and the shades obtained are described, together with those of morin, for the sake of comparison :

	Chromium.	Aluminium.	Tin.	Iron.
Colouring matter of <i>Delphinium Consolida</i>	Brownish-yellow.	Yellow.	Lemon-yellow.	{ Deep olive-brown.
Morin .....	Olive-yellow.	Dull yellow.	Bright yellow.	{ Deep olive-brown.

In this respect, therefore, these colouring matters are almost identical, morin, however, being stronger to a slight extent.

The reactions of the colouring matter  $C_{15}H_{10}O_6$  harmonised closely with those given by Gordin (*Diss., Berns*) to *kampherol*, which he prepared from the monomethyl ether, kampheride, contained in galanga root (*Alpinia officinarum*). Thus the melting points of these compounds and those of their acetyl derivatives are practically identical, and the decomposition products are the same in both cases. To kampherol, Kostanecki has given the following constitution as probable (*Ber.*, 1901, 34, 3723) :



it being thus the connecting link between apigenin (*Trans.*, 1897, 71, 805) and quercetin. An unsuccessful attempt was made to procure a copy of Gordin's dissertation, but an extract evidently taken from it is given in *Der Chemie der natürlichen Farbstoffe*, 1900, p. 80. In this description, the only distinction of importance between the colouring matter under discussion and kampherol is to be found in the account given of the dyeing properties of the latter, regarding which the following sentence occurs: "Kämpferid sowohl wie Kämpferol färben Thonerdebeize schwach gelb an." As this is not in harmony with the above results, it was necessary to prepare some kampheride, and from this kampherol.

In isolating the constituents of galanga root, its ethereal extract was treated according to the method given by Ciamician and Silber (*Ber.*, 1899, 32, 861). Possibly the quality of the root varies, for the process employed by these authors was not entirely satisfactory. Thus the extract diluted with benzene gave a semi-crystalline precipitate, devoid of kampheride, which, after purification, melted at 292—295°, gave an acetyl compound melting at 175—176°, and was identical with the galangin monomethyl ether described by Testoni (*Gazzetta*, 1900, 30, ii, 327—329). The filtrate, on addition of light petroleum, deposited a brown tar, and this, on solution in hot chloroform, gave, on cooling, a precipitate containing kampheride and galangin, which were

separated by fractional crystallisation from alcohol. The kampheride thus obtained melted at 223—226°, and the kampherol prepared from it at 271—272°. The latter possessed well marked dyeing properties, identical in all respects with those of the colouring matter of *Delphinium Consolida*, and there can be no doubt that the two are identical.

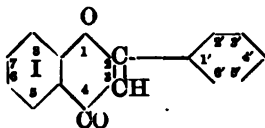
A study of the acetyl derivative of kampherol from kampheride showed that this, when crystallised from methyl alcohol, had the same double melting point as that described above; further, the acetyl compound of kampherol obtained from robinin (this vol., p. 475) behaved similarly. It thus appears that this is a definite property of the substance.

Molisch and Goldschmiedt (*Monatsh.*, 1901, 22, 679) have recently described a colouring matter, scutellarein, which exists in the form of its glucoside, scutellarin, in the *Scutellaria altissima*. This has the same formula and general reactions as kampherol, and yields the same decomposition products, but melts at above 300°. To be certain that the melting point of kampherol here given was correct, a sample was treated in numerous ways; for example, with hydriodic acid, then converted into its sulphate and into its potassium compound, then crystallised from acetic acid, &c., but the melting point was practically unaltered, the final product melting at 276—277°. Scutellarein and kampherol, therefore, cannot be identical.

Attempts to isolate the glucoside of kampherol which exists in the *Delphinium Consolida* have not yet been successful, but the results show that this compound is not robinin.

### *The Dyeing Properties of some Members of the Flavone Group.*

Being in possession of the galangin prepared as above, we studied its dyeing properties, with the object of gaining further insight into the functions in this respect of the various hydroxyl radicles contained in the compounds previously studied. Woollen cloth similarly mordanted (mordanted calico, so frequently employed by others, is of little service for comparing the members of this group) was employed in each case, and the experiments were carried out, as far as possible, in an identical manner. The positions of the hydroxyl radicles are indicated by the numbers in the following formula :



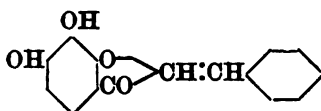


	Chromium.	Aluminium.	Tin.	Iron.
Chrysin, $C_{15}H_8O_2(OH)_2$ ..... [5:7]	Yellow, faint orange tint.	Pale yellow.	Undyed.	Pale chocolata.
Apigenin, $C_{15}H_8O_2(OH)_3$ ... [5:7:4']	„	Pale yellow, slightly stronger.	„	Chocolate- brown.
Luteolin, $C_{15}H_8O_2(OH)_4$ ... [5:7:4':5']	Brown- orange.	Orange- yellow.	Bright yellow.	Olive-black.
Galangin, $C_{15}H_8O_2(OH)_3$ ... [5:7:3]	Olive yellow.	Yellow.	Lemon- yellow.	Deep olive.
Kampherol, $C_{15}H_8O_2(OH)_4$ . [5:7:3:4']	Brown- yellow.	„	Lemon- yellow.	Deep olive- brown.
Morin, $C_{15}H_8O_2(OH)_6$ ..... [5:7:3:2':4']	Olive-yellow.	Dull yellow.	Bright yellow.	Deep olive- brown.
Quercetin, $C_{15}H_8O_2(OH)_5$ ... [5:7:3:3':4']	Red-brown.	Brown- orange.	Bright orange.	Olive-black.
Myricetin, $C_{15}H_8O_2(OH)_6$ ... [5:7:3:3':4':5']	„	„	Bright red- orange.	Olive-black.
Rhamnetin, $C_{15}H_8O_2(OH)_4$ . [5:3:3':4']	„	„	Bright orange.	Deep olive.
Fisetin, $C_{15}H_8O_2(OH)_4$ ..... [7:3:3':4']	„	Reddish- brown-orange	Bright red- orange.	Olive-black.

Certain other colouring matters, as apigenin monomethyl ether (Trans., 1900, 77, 430), kampheride, galangin monomethyl ether, isorhamnetin, rhamnazin, &c., could be added to this list, but are omitted, as the above form a complete series. Only five of these colouring matters, luteolin, fisetin, rhamnetin, quercetin, and myricetin, contain two hydroxyl radicles in the ortho-position relatively to one another, a condition which Liebermann and Kostanecki noted to be essential in the case of the anthraquinone dyestuffs.

Although this factor, doubtless, exercises a strengthening effect in the dyestuffs of the flavone series, it is not a necessity, as is specially evident in the cases of morin and kampherol, the former of which, occurring as it does in old fustic, is still most extensively employed in the dyeing industry. An interesting point is the marked increase in tinctorial property associated with the presence of hydroxyl in position 3, as is at once observed between chrysin and galangin, apigenin and kampherol, and no doubt exists between luteoflavin,  $C_{15}H_8O_2(OH)_4$  [5:7:2':4'] (Dunstan and Henry, *Proc. Roy. Soc.*, 1901, 68, 374), and morin; this is again to be seen in the case of luteolin and quercetin, for its presence in the latter gives strength and redness to the shades. It will be noted from the above examples that a multiplication of hydroxyl radicles in the flavone series does not by any means exert such a marked tinctorial effect as is observed in the anthraquinone group (compare, for instance, alizarin, anthragallol, and alizarin-cyanine R); this is evident by the almost identical character of the shades given by apigenin and chrysin, by fisetin,

quercetin, rhamnetin, and myricetin, and by galangin, kampherol, and morin. The introduction of hydroxyl in the positions 4' and 4':2', in galangin, with the respective formation of kampherol and morin, certainly exerts some strengthening effect, but on the other hand fisetin, quercetin, and myricetin do not materially differ in strength of shade. It is likely, however, that hydroxyl radicals in ortho-positions relatively to one another in the nucleus I (p. 589) would exert a more marked effect on the shade, for the benzylideneanhydroglycogallol,



(Friedländer and Rudt, *Ber.*, 1896, 29, 878), a member of a closely allied group, yields powerful and characteristic colours. The dyeing properties of these and other phenolic compounds are intimately connected with their property of forming monosubstituted salts (*Trans.*, *loc. cit.*); this question will be discussed in a further communication, which it is hoped will be laid before the Society at an early date.

A preliminary investigation of the flowers of *Prunus spinosa* has shown that these contain an apparently new colouring matter, which in its general reactions resembles kampherol. This will be further investigated.

The authors express their thanks to the Research Fund Committee of the Chemical Society for a grant which has been in part employed to cover the expenses of this research.

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### LXIII.—*Synthesis of Imino-ethers. N-Arylbenzimidino-ethers.*

By G. D. LANDER.

ALTHOUGH aryl substituted benzimidino-ethers may be prepared from the benzoylated amines by means of silver oxide and alkyl iodides (*Trans.*, 1901, 79, 698), the yields are poor, partly owing to the relatively sparing solubility of the benzoyl compounds. It therefore became desirable to find a more economical process, by which imino-ethers of this class can be prepared in larger quantities for the purpose of

studying some of their properties, and especially a process in which the chance of the simultaneous formation of both N- and O-ethers, which seems to be characteristic of methylation by means of silver oxide, is either absent or at a minimum.

This 'molecular rearrangement in the course of synthesis' of methyl ethers by means of silver oxide and methyl iodide is not so characteristic of the benzoylated as of the acetylated arylamines. Whilst the methylation of aceto-*o*-toluidide by this process leads to the formation of about equal proportions of the isomeric ethers, and that of aceto-*p*-toluidide to the almost exclusive formation of the N-ether, with benz-*o*-toluidide scarcely any N-ether is formed, and with benz-*p*-toluidide about equal amounts of the two isomerides are produced.

The possibility of preparing imino-ethers from imide chlorides and sodium alkyl oxides, in accordance with the general reaction,



appeared most promising; moreover, on *a priori* grounds, it was probably a reaction of simple replacement, and consequently one in which molecular rearrangement would not occur. The application of this mode of synthesis is not new. It has been used, among other instances, by Hantzsch (*Ber.*, 1893, 26, 927) in the preparation of N-phenylbenzimidino-phenyl ether, and by Lengfeld and Stieglitz (*Amer. Chem. J.*, 1895, 17, 98) in the formation of ethyl isocarbanilide from carbodiphenylimide monohydrochloride (the imide chloride corresponding to diphenylurea). I have found that the reaction is very well adapted to the synthesis of aryl substituted benzimidino-ethers, and that methyl ethers are obtainable with as great ease as the ethyl derivatives, no isomerisation appearing to take place.

Our knowledge of the imide chlorides is due mainly to Wallach (*Annalen*, 1876, 184, 1), who has shown how they are derived from substituted amides by the action of phosphorus pentachloride, the group  $-CO \cdot NH-$  giving first  $-CCl_2 \cdot NH-$  and then  $-CCl:N-$ . The use of imide chlorides derivable from amides, as distinguished from compounds such as  $C_6H_5 \cdot N:CCl \cdot NH \cdot C_6H_5$ ,  $C_6H_5 \cdot N:CCl_2$ , and  $N:C \cdot Br$ , which, although belonging to the same category, are not usually prepared directly from an amido-compound, is restricted as a practical method of imino-ether synthesis, apparently, to the benzoylated amines. Its application to the preparation of phenyl, *o*-tolyl, and *p*-tolyl substituted benzimidino-ethers is described in this paper.

Acetanilide imide chloride is difficult to prepare, as it passes at about 50° into the chlorinated base  $C_{16}H_{15}N_2Cl$ , which is resolved by alcohol into two mols. of acetanilide (Wallach, *loc. cit.*, 86).

In the hope that sodium ethoxide might cause the resolution of this compound into molecular proportions of acetanilide and N-phenyl-

acetimino-ethyl ether, I caused a solution of sodium in ethyl alcohol to act on a benzene solution of the base; the main product was, however, diphenylethenylamidine, probably formed by the conversion of the chlorinated base by the action of the ethoxide into the chlorine-free base  $C_{16}H_{14}N_2$ , and the subsequent change of this into the amidine (compare Wallach, *loc. cit.*).

The imide chloride of *s*-benzoylphenylhydrazine (Pechmann, *Ber.*, 1894, 27, 322) gave, on treatment in benzene solution with alcoholic sodium ethoxide, a deep brownish-red, tarry substance, possibly a formazyl derivative, which was not further examined.

## EXPERIMENTAL.

### I. *N*-Phenylbenzimino-ethers.

#### *Formation of N-Phenylbenzimino-ethyl Ether from Benzanilide Imide Chloride*

In the earlier experiments on the formation of this imino-ether, the benzanilide imide chloride, prepared as directed by Wallach (*loc. cit.*), was purified by distillation in a vacuum, a procedure subsequently found to be unnecessary. In the first instance, the action of dry sodium ethoxide on a solution of the imide chloride in light petroleum was tried. The liquid acquired a dark brown colour, but after several hours' boiling the reaction was incomplete. Most of the solvent having been distilled off, the residue was extracted with water, and on distillation in a vacuum, a small quantity of a yellowish-brown liquid having all the properties of *N*-phenylbenzimino-ethyl ether was obtained. The employment of an alcoholic solution of the ethoxide leads, however, to the production of imino-ether, both rapidly and in excellent yield. The method of preparation finally adopted may be described.

Fifty grams of benzanilide and 51 grams of phosphorus pentachloride were fused together, warmed gently until the evolution of hydrogen chloride had ceased, and the phosphorus oxychloride distilled off in a vacuum. By extraction of the residue with light petroleum and filtration, a somewhat opalescent but practically pure solution of the imide chloride was obtained.

A solution of 5.5 grams of sodium in the requisite amount of ethyl alcohol was added to this solution, which was cooled, the addition requiring only a few minutes, and the resulting product having an alkaline reaction. The sodium chloride was extracted by water, the petroleum solution filtered from some benzanilide, dried with calcium chloride, and the product distilled in a vacuum. By this means, 41.5 grams of *N*-phenylbenzimino-ethyl ether, boiling at 175—177°

under 16 mm. pressure, was obtained. The boiling point is  $172^{\circ}$  under 15 mm.,  $168\text{--}170^{\circ}$  under 14 mm., and  $220\text{--}230^{\circ}$  under from 20 to 30 mm. pressure :

0.128 gave 7 c.c. moist nitrogen at  $16^{\circ}$  and 762 mm.  $N = 6.37$ .

$C_{15}H_{15}ON$  requires  $N = 6.22$  per cent.

The compound showed all the properties of this imino-ether, readily undergoing hydrolysis by dilute mineral acids into aniline and ethyl benzoate, and giving a sticky hydrochloride which evolved ethyl chloride on being warmed or kept, leaving a residue of benzanilide.

A small quantity of a substance of high boiling point was invariably formed in this as in other similar reactions. It remained as a glassy mass after the imino-ether had been distilled. Unless in a state approaching purity, it was exceedingly difficult to crystallise, in spite of its high melting point. The formation of this bye-product was considerably increased at the expense of the imino-ether by adding alcohol drop by drop to a boiling solution of the imide chloride, to which the calculated amount of sodium wire had been added, until the latter was dissolved; but thus prepared, the substance resisted all attempts at crystallisation. The united residues of several imino-ether preparations were crystallised from a mixture of chloroform and light petroleum, forming dense, pale yellow, prismatic crystals melting at  $170\text{--}172^{\circ}$  without decomposition. On analysis :

0.1486 gave 0.4515  $CO_2$  and 0.0798  $H_2O$ .  $C = 82.86$  ;  $H = 5.96$ .\*

0.1278 „ 0.3874  $CO_2$  „ 0.0660  $H_2O$ .  $C = 82.67$  ;  $H = 5.73$ .

0.1560 „ 10 c.c. moist nitrogen at  $13^{\circ}$  and 768 mm.  $N = 7.64$ .

0.1330 „ 8.4 c.c. „  $12^{\circ}$  „ 768 mm.  $N = 7.56$ .

A cryoscopic determination of the molecular weight in acetic acid solution gave the value 372.

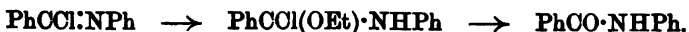
These data agree best with the formula  $C_{26}H_{20}ON_2$ , which requires  $C = 82.97$  ;  $H = 5.32$  ;  $N = 7.44$  per cent.

This is the composition of *benzoyldiphenylbenzenylamidine*,  $PhC:NPh \cdot N(COPh)Ph$ , with which the substance proved to be identical. By boiling it with moderately concentrated sulphuric acid, it was resolved into benzoic acid and diphenylbenzenylamidine. The benzoyl derivative of the latter compound, prepared either by allowing benzoyl chloride and the base to interact in benzene solution, or by the Schotten-Baumann method, possessed the same crystalline appearance, colour, and melting point as the compound from the imide chloride, and gave  $N = 7.56$ , instead of the calculated 7.44 per cent.

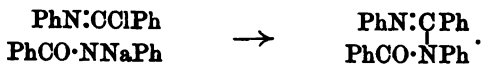
It is exceedingly probable that the formation of benzoylated amidine from imide chloride takes place in the following manner. The

\* Analysed by Mr. G. Clarke, A.I.C.

alcohol used as a solvent for the sodium ethoxide causes a partial decomposition of the benzanilide imide chloride into benzanilide,



By the action of the sodium ethoxide, sodiobenzanilide would be formed and yield the benzoylated amidine thus,



*N-Phenylbenzimidino-methyl Ether.*

By the interaction of a solution of the required amount of sodium in methyl alcohol and a light petroleum solution of benzanilide imide chloride from 25 grams of benzanilide, 18·5 grams of the imino-ether boiling at 157—158° under 12 mm. pressure were obtained :

0·1858 gave 10·8 c.c. moist nitrogen at 18° and 770 mm.  $N = 6·79$ .

$\text{C}_{14}\text{H}_{18}\text{ON}$  requires  $N = 6·63$  per cent.

The compound was resolved by dilute mineral acids into aniline and methyl benzoate, and by anhydrous ethereal hydrogen chloride into benzanilide and methyl chloride.

This imino-ether has been prepared by Wislicenus and Goldschmidt (*Ber.*, 1900, 33, 1471) by an application of Lossen's method (*Annalen*, 1891, 265, 138). They give 145—150° under 8 mm. pressure as its boiling point.

Benzoyldiphenylbenzenylamidine was a bye-product of the synthesis, and in addition a small quantity of diphenylbenzenylamidine, melting at 143—145°, appeared to have been formed.

*Methylation of Benzanilide by Methyl Iodide and Silver Oxide.*—This methylation was carried out for the purpose of comparison with the process of alkylation of acetylarylamines by the same method. The product obtained from 10 grams of benzanilide, 35 grams of silver oxide, and 42 grams of methyl iodide in 50 c.c. of benzene after 3 hours' boiling, consisted of 5 grams of *N*-phenylbenzimidino-methyl ether boiling at 163° under 11 mm. pressure, and identified in the usual way, some unaltered benzanilide, and between 3 and 4 grams of benzoylmethylaniline. The last named compound was present in the part of the product which boiled between 180° and 190° under 9 mm. pressure, and was not obtained solid. It was freed from imino-ether by steam distillation with dilute hydrochloric acid, the unaltered oil separated, hydrolysed with moderately concentrated sulphuric acid, and the methylaniline thus obtained identified by means of its acetyl derivative.

*N-Phenylbenziminopropyl Ether.*

This compound was prepared by the action of a solution of 3 grams of sodium in *n*-propyl alcohol on the light petroleum extract of the imide chloride from 25 grams of benzanilide. It boiled at 180—182° under 13 mm., and at 177—179° under 11 mm. pressure. After three distillations, 10 grams of the desired product, displaying the usual reactions of an imino-ether, were obtained :

0.1872 gave 9.2 c.c. moist nitrogen at 9° and 760 mm.  $N = 5.89$ .

$C_{16}H_{17}ON$  requires  $N = 5.85$  per cent.

II. *N-o-Tolylbenziminoothers.**N-o-Tolylbenziminooethyl Ether.*

A light petroleum solution of the imide chloride from 20 grams of benz-*o*-toluidide was treated with 3 grams of sodium dissolved in ethyl alcohol in the manner already described. After three distillations, 14 grams of imino-ether boiling at 179—180° under 15 mm. pressure were obtained :

0.2344 gave 11.8 c.c. moist nitrogen at 9° and 749 mm.  $N = 5.95$ .

$C_{16}H_{17}ON$  requires  $N = 5.85$  per cent.

As in the similar reaction between sodium ethoxide and benzanilide imide chloride, a residue of high boiling point remained after distillation of the imino-ether. It displayed, however, less tendency to crystallise, and in view of the very probable similarity between it and the product already dealt with, was not further examined. The same remark is true of the products obtained from the imide chloride of benz-*p*-toluidide.

*N-o-Tolylbenziminomethyl Ether.*

The imide chloride from 20 grams of benz-*o*-toluidide, by interaction with the requisite amount of sodium in methyl alcoholic solution, gave 15 grams of the imino-ether boiling at 173° under 15 mm. pressure :

0.1495 gave 0.4375  $CO_2$  and 0.0925  $H_2O$ .  $C = 79.81$  ;  $H = 6.86$ .\*

$C_{15}H_{15}ON$  requires  $C = 80.00$  ;  $H = 6.66$  per cent.

*Methylation of Benz-o-toluidide by Methyl Iodide and Silver Oxide.*  
—Interaction between 35 grams of silver oxide, 42 grams of methyl iodide, and 15 grams of benz-*o*-toluidide dissolved by the aid of 60 c.c. of benzene, resulted in the formation of 8 grams of *N-o*-tolylbenziminomethyl ether boiling at 170—171° under 11 mm. pressure. Nearly all

\* Analysed by Mr. G. Clarke, A.I.C.

the remaining product was unaltered toluidide, but after this had been removed as completely as possible by crystallisation from aqueous alcohol, a small quantity of a thick oil remained. After separation, hydrolysis with sulphuric acid and liberation of the base, a sufficient quantity was obtained to give Liebermann's reaction, thus showing that benz-*o*-methyltoluidide was a product of the reaction.

The influence of orientation on the properties of the substituted benzimino-ethers is notably less well defined than in the cases of the analogous substituted acetimino-compounds, indeed, scarcely any influence can be detected by the methods applicable to the latter substances (compare Trans., 1901, 79, 693). When cold dilute hydrochloric acid is added to the *o*-tolylbenzimino-ethers, solution occurs, but the almost instantaneous appearance of a turbidity indicates the commencement of the characteristic hydrolysis, and a platinichloride cannot be prepared, even by the addition of alcoholic platonic chloride to an alcoholic solution of the base. The hydrochlorides could not be prepared by means of anhydrous ethereal hydrogen chloride.

I take this opportunity of making a correction and addition to the description of the substituted acetimino-ethers formerly described (*loc. cit.*). When freshly distilled acetyl chloride is added to a light petroleum solution of N-*o*-tolylacetimino-ethyl ether, an oil is precipitated, which solidifies on rubbing to colourless needles, fusing with copious evolution of gas at 109—110° and leaving a residue of aceto-*o*-toluidide. These needles are the hydrochloride of the imino-ether in a purer state than the amorphous salt melting at 90—91° previously prepared from the base by means of ethereal hydrogen chloride. On analysis, the crystalline salt gave Cl = 16.42 instead of 16.62 per cent. Moreover, by the same mode of treatment N-phenylacetimino-ethyl ether, the hydrochloride of which I have not formerly prepared, gives that salt in a crystalline state; it melts evolving gas at 100°. This result of the action of acetyl chloride is easily explicable, bearing in mind the difficulty of freeing this substance from traces of hydrochloric acid. The reagent, however, has not proved suitable for the preparation of the hydrochlorides of substituted benzimino-ethers.

The only respect, then, in which orientation seems to influence the formation of the aryl substituted benzimino-ethers is displayed in the extent to which the isomeric N-methyl homologues are formed in methylation by means of silver oxide (*loc. cit.*, 696).

### III. N-*p*-Tolylbenzimino-ethers.

#### N-*p*-Tolylbenzimino-ethyl Ether.

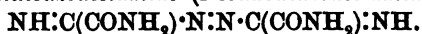
The imide chloride corresponding to 20 grams of benz-*p*-toluidide gave, on treatment with sodium ethoxide and four distillations of the



*Preparation of Ethyl Diazoacetate.*

The following method will be found most convenient where large quantities of the ester are required. Five grams of sodium acetate are dissolved in 2 litres of water in a 10 litre separating funnel; to this solution, 1 kilogram of the finely powdered hydrochloride of ethyl aminoacetate (for the preparation of this compound see Hantzsch and Silberrad, *loc. cit.*, p. 70) is added, and then 750 grams of sodium nitrite. The mixture is shaken until the temperature has fallen to about 0°. Five c.c. of 10 per cent. sulphuric acid and  $\frac{1}{2}$  litre of ether are then added and the whole again well shaken. During this period, the gradual solution of the still undissolved salts cools the mixture and prevents the reaction from becoming too violent. As soon as the action slackens, the ethereal solution of ethyl diazoacetate is run off, fresh ether added, and 10 per cent. sulphuric acid run in from time to time in small quantities until red fumes are evolved. The ethereal solution is then run off, added to that already obtained, washed with small quantities of dilute sodium carbonate solution until the washings assume a deep yellow colour and have an alkaline reaction. The ethereal solution is dried by shaking with fused calcium chloride, and freed from ether on the water-bath. The yield amounts to 770 grams or 94.7 per cent. of the calculated quantity.

*Iminoazoacetamide (Pseudodiazoacetamide),*



Iminoazoacetamide is obtained as a clear yellow, crystalline powder when the purified ammonium salt (see below), dissolved in the least possible quantity of water at 0°, is precipitated with an excess of 80 per cent. acetic acid also cooled to 0°. The precipitated amide, after being washed with water and dried on a porous plate in a vacuum, decomposes violently at 135—136°. On analysis, the following results were obtained:

Found: C = 28.44; H = 3.70; N = 49.59.

(C<sub>2</sub>H<sub>5</sub>ON<sub>3</sub>)<sub>x</sub> requires C = 28.23; H = 3.53; N = 49.41 per cent.

The ammonium salt, NH·C(CONH<sub>2</sub>)·N·N·C(CONH<sub>2</sub>)·N(NH<sub>4</sub>).—After many experiments, the following method of preparation was found to give the best results. One hundred and twenty grams of methyl diazoacetate are added to 1 litre of aqueous ammonia, saturated at 0°, and allowed to stand in a well-closed bottle for 14 days at -15°. The separated crystals are then filtered off and the mother liquor again allowed to stand for 14 days at -15°, when a further supply of crystals

separates out. These are reduced to the finest possible powder and well washed with small quantities of ice-cold water, whereby traces of diazoacetamide and ammonium bisdiazooacetate are removed. The resulting product, on drying over sulphuric acid, loses no ammonia, and melts with decomposition at 155—157°. On analysis, the following figures were obtained :

Calculated for (C <sub>2</sub> H <sub>3</sub> ON <sub>2</sub> ) <sub>2</sub> NH <sub>3</sub> .	Found. Curtius and Lang.	Silberrad.	Calculated for (C <sub>2</sub> H <sub>3</sub> ON <sub>2</sub> ) <sub>2</sub> 2NH <sub>3</sub> .
C = 25·67	26·49	26·01	25·00
H = 4·81	4·92	4·98	5·19
N = 52·41	52·97	52·45	53·28

These results agree more closely with the formula (C<sub>2</sub>H<sub>3</sub>ON<sub>2</sub>)<sub>2</sub>NH<sub>3</sub> than with (C<sub>2</sub>H<sub>3</sub>ON<sub>2</sub>)<sub>2</sub>2NH<sub>3</sub>, a fact previously noticed by Curtius (*Ber.*, 1885, 18, 1291); he was, however, under the misapprehension that all the polymerides of diazoacetic acid were termolecular, a mistake for which an erroneous molecular weight determination by E. Wiedemann (*J. pr. Chem.*, 1888, [ii], 38, 541) is chiefly responsible.

The silver salt, 3NH<sub>2</sub>C(CONH<sub>2</sub>)·N<sub>2</sub>N·C(CONH<sub>2</sub>)·NAg + AgNO<sub>3</sub>.—The silver salt is obtained as a voluminous yellow precipitate by the addition of silver nitrate to a solution of the ammonium salt. The precipitate is extremely sensitive to actinic rays, and can be obtained pure only by working entirely by red light; on warming, it blackens immediately.

After drying in a vacuum over sulphuric acid in the dark until the weight became constant, the following results were obtained on analysis :

Calculated for C <sub>12</sub> H <sub>15</sub> O <sub>9</sub> N <sub>15</sub> Ag <sub>4</sub> .	Found. Curtius and Lang.	Silberrad.	Calculated for C <sub>3</sub> H <sub>3</sub> N <sub>4</sub> (Nag) <sub>2</sub> (CONH <sub>2</sub> ) <sub>2</sub> ·1½H <sub>2</sub> O.
C = 14·39	—	14·29	14·52
H = 1·50	—	1·78	2·02
N = 26·57	25·58	26·00	25·40
Ag = 43·16	43·57, 43·81	43·62	43·55

It will be seen that the silver and the nitrogen, which were the only constituents estimated by Curtius and Lang, agree equally well with either formula; the carbon and hydrogen, however, leave no doubt as to which is correct.

This complex formula evidently represents a double salt, thus :



which is strictly analogous to other polymeric products of diazoacetic acid (Hantzsch and Silberrad, *loc. cit.*, p. 67).

*Action of Nitrogen Trioxide (a). Preparation of Bisazoxyacetic Acid.*—Twenty grams of the finely powdered amide were placed in a dry flask, cooled to 0°, and subjected to the action of nitrogen trioxide (prepared

from nitric acid of sp. gr. 1.38 and arsenious acid) until a sample of the product dissolved completely in cold water. The contents of the flask, which had assumed a carmine-red colour, were placed on a porous plate over caustic potash in a vacuum. On heating, the product decomposed below  $100^{\circ}$ , and on analysis proved to be very impure (found  $N = 30.4$ ; calculated for  $C_4H_4O_6N_4$ ,  $N = 27.4$  per cent). Consequently the product was converted into the sodium salt by neutralising it, suspended in ice-cold water, with dilute caustic soda also cooled to  $0^{\circ}$ . To the crude sodium salt so obtained, a few drops of dilute nitric acid and then silver nitrate solution were added, when the characteristic dark green silver salt of bisazoxyacetic acid was precipitated. This, on analysis, proved still to be contaminated with a substance richer in nitrogen than bisazoxyacetic acid. The product was therefore suspended in water and saturated with sulphuretted hydrogen at  $0^{\circ}$ , following the method described by Hantzsch and Lehmann (*loc. cit.*, p. 3674) for the reduction of bisazoxyacetic acid to bisdiazaoacetic acid.

The product, freed from sulphur by extraction with cold absolute alcohol, was shaken with excess of ammonia, filtered, and the filtrate cooled to  $0^{\circ}$  and precipitated with dilute sulphuric acid. The precipitate, after drying on a porous plate, melted at  $150^{\circ}$ , and on analysis proved to be bisdiazaoacetic acid:

Found  $N = 27.01$ .  $C_2H_2N_4(CO_2H)_2, 2H_2O$  requires  $N = 26.92$  per cent.

Hence it is evident that the product of the action of nitrogen trioxide on dry iminoazoacetamide was principally bisazoxyacetic acid.

(b) *Preparation of Triazole*.—Five grams of iminoazoacetamide suspended in ice-cold water were saturated with nitrogen trioxide. The solution assumed a carmine-red colour (indicative of the formation of bisazoxyacetic acid), and on evaporation on the water-bath yielded a yellowish, crystalline mass; this, after repeated recrystallisation from absolute alcohol, gave a product melting at  $138^{\circ}$ , which on analysis proved to be triazole nitrate:

Found,  $C = 18.33$ ;  $H = 3.22$ ;  $N = 42.30$ .

$C_2H_3N_3.HNO_3$  requires  $C = 18.18$ ;  $H = 3.03$ ;  $N = 42.42$  per cent.

*Action of Caustic Soda.* (a) *Preparation of Sodium Salt* (†).—Dilute cold caustic soda solution decomposed the ammonium salt with evolution of ammonia, giving the characteristic intense yellow colour of the salts. On evaporation in a vacuum, decomposition occurred, hence the sodium salt could not be isolated.

(b). *Formation of Bisdiazaoacetic Acid*.—Ten grams of the finely powdered substance were thrown, little by little, into a solution of 10 grams of caustic soda in 25 c.c. of water previously heated to  $90^{\circ}$ . At each addition, considerable rise of temperature and violent evolution

of ammonia occurred. The contents of the flask assumed a deep yellow colour and became semi-solid owing to the separation of sodium bisdiazooacetate.

The product was washed with alcohol, recrystallised from water, and decomposed with dilute sulphuric acid, whereby bisdiazooacetic acid was obtained. This was identified by its melting point,  $152^{\circ}$ , the colour reaction of its silver salt (Hantzsch and Silberrad, *loc. cit.*, p. 73), and by a nitrogen determination:

Found N = 26.99;  $C_2H_2N_4(CO_2H)_2 \cdot 2H_2O$  requires N = 26.92 per cent.

*Action of Barium Hydroxide. Preparation of Iminoazoacetic Acid.*—The addition of barium acetate to a concentrated solution of ammonium iminoazoacetamide produced no precipitate. If, however, the solution of the ammonium salt be warmed with baryta water, a pale yellow precipitate forms and ammonia is evolved.

The product is probably barium iminoazoacetate,  $\begin{array}{c} \text{N} \cdot \text{C}(\text{NH}) \cdot \text{CO}_2 \\ | \\ \text{N} \cdot \text{C}(\text{NH}) \cdot \text{CO}_2 \end{array} > \text{Ba}$ . After washing and drying over sulphuric acid, it gave the following result on analysis:

Found N = 18.36; Ba = 44.82.

$C_4H_2O_4N_4Ba$  requires N = 18.28; Ba = 44.52 per cent.

Attempts to isolate the free acid have not yet been successful. Dilute sulphuric acid appears to bring about decomposition; its action was studied as follows: To 2 grams of the barium salt suspended in ice-cold water, a very slight excess of dilute sulphuric acid was added. On evaporation, only oxalic acid and hydrazine could be detected. The oxalic acid was separated as the calcium salt, which, after drying at  $100^{\circ}$ , gave the following result on analysis:

Found Ca = 27.11;  $C_2O_4Ca \cdot H_2O$  requires 27.40 per cent.

The hydrazine was isolated as benzyldieneazine, which after crystallisation from alcohol melted at  $93^{\circ}$  and gave the following result on analysis:

Found N = 13.50;  $C_{14}H_{12}N_2$  requires 13.46 per cent.

*Action of Ammonia. Preparation of Diazoacetamide and isoDiazoacetamide.*—Five grams of the ammonium salt were dissolved in 100 c.c. of 10 per cent. ammonia and the solution allowed to evaporate over soda lime in a vacuum. A very porous brown product resulted, which on exposure to air rapidly shrank to a dark brown, resinous mass. If, however, the porous substance be treated with dilute acetic acid (without opening the desiccator), complete solution occurs with evolution of nitrogen (showing thereby the absence of any unaltered iminoazoacetamide). On addition of benzaldehyde to this solution, a crys-

talline magma rapidly forms. After recrystallisation, the product melted at  $93^{\circ}$ , and on analysis proved to be benzylideneazine:

Found C = 80.66; H = 6.00; N = 13.54.

$C_{14}H_{12}N_2$  requires C = 80.77; H = 5.77; N = 13.46 per cent.

*Constitution of isoDiazoacetamide.*—The stability of the tetrazine ring disarms any suggestion that this readily decomposable product is a tetrazine derivative. Indeed, its ready solubility in water points to its being an isomeride rather than a polymeride of diazoacetamide. Further, the readiness with which it yields hydrazine indicates that it is not a true derivative of diazoacetic acid, so that it appears probable that the compound is isodiazoacetamide, or, more likely, its ammonium salt,  $CONH_2 \cdot C \begin{smallmatrix} \nearrow N(NH_4)^* \\ \searrow N \end{smallmatrix}$ .

The evolution of nitrogen above referred to seems to indicate the presence of derivatives of normal diazoacetic acid. The product of the action of ammonia on a further quantity of iminoazoacetamide was therefore exposed to the air, the resinous mass extracted with cold absolute alcohol, and the yellow solution allowed to evaporate in a vacuum, whereby beautiful, yellow, prismatic crystals were obtained. After recrystallisation from warm absolute alcohol, the compound melted at  $114^{\circ}$  with violent decomposition and proved to be diazoacetamide.

Found N = 49.00;  $C_2H_3ON_2$  requires N = 49.41 per cent.

The yield is small, being about 0.4 gram from 10 grams of iminoazoacetamide; the chief product of the reaction is evidently isodiazoacetamide.

#### *Bisdiazoacetamide.*

The method described by Curtius and Lang (*J. pr. Chem.*, 1888, [ii], 38, 543) from ethyl bisdiazoacetate (Hantzsch and Silberrad (*loc. cit.*, p. 72) is by far the most convenient for the preparation of the substance. Unlike iminoazoacetamide, bisdiazoacetamide forms no salts.

*Action of Nitrogen Trioxide.*—Treated as described in the case of iminoazoacetamide, this substance gave rise to bisazoxyacetic acid both when dry and in aqueous suspension. The product was identified

\* Since the completion of this part of the work, a paper has appeared by Hantzsch and Lehmann (*Ber.*, 1901, 34, 2510), in which they describe a precisely similar product as resulting from the action of ammonia on ethyl isodiazoacetate. This appears to be a strong argument in favour of the above constitution; it must, however, be stated that normal ethyl diazoacetate can also be almost quantitatively converted into the same product by the direct action of ammonia. This will be discussed in a subsequent communication.

by its characteristic green silver salt, which, however, could not be obtained pure from this source, and was therefore further identified by reduction with sulphuretted hydrogen, whereby bisdiazooacetic acid was obtained melting at  $152^{\circ}$ . On analysis:

Found  $N = 26.89$ ;  $C_2H_2N_4(CO_2H)_2 \cdot 2H_2O$  requires  $N = 26.92$  per cent.

Neither in aqueous suspension nor in the dry state could any triazole nitrate be obtained, although 50 grams of the substance in aqueous suspension were treated with nitrogen trioxide.

On evaporation on the water-bath, large quantities of ammonium nitrate separated. The product was dissolved in water and calcium acetate added, whereby a precipitate of the oxalate was obtained.

Found  $Ca = 26.87$ ;  $C_2O_4Ca \cdot H_2O$  requires  $Ca = 27.40$  per cent.

The filtrate, after removal of calcium, was rendered neutral and treated with copper acetate; no precipitate of copper triazole formed, although the solution was allowed to stand for several weeks.

*Action of Alkalis.*—As already observed by Curtius and Lang (*J. pr. Chem.*, 1888, [ii], 38, 344), bisdiazooacetamide is easily saponified by aqueous alkalis in a perfectly normal manner. Aqueous ammonia is without action on the amide.

#### *s-N-Dihydrotetrazinedicarboxylamide.*

The instructions given for the preparation of *n*-dihydrotetrazinedicarboxylic acid (Hantzsch and Silberrad, *loc. cit.*, p. 77) are not clear owing to the accidental omission of an important sentence. The directions should be as follows: 100 c.c. of ethyl diazoacetate are run into a solution of 160 grams of caustic potash in 120 c.c. of water, as in the preparation of potassium bisdiazooacetate (*J. pr. Chem.*, 1888, [ii], 38, 534). A solution of 57 grams of caustic potash in 93 c.c. of water is then added, and the resulting semi-solid mass well shaken and heated on the water-bath in an open flask until the greater part of the alcohol formed by the saponification of the ethyl diazoacetate has been driven off. The flask is then attached to a reflux condenser, and the heating continued until an almost colourless, thick liquid results, a process which requires about 48 hours. This product is shaken with alcohol until the bulk of the caustic alkali has been removed. The thick, oily residue is then allowed to stand in the cold, when the greater part of the *N*-dihydrotetrazinedicarboxylic acid separates out as the potassium salt. The crude product is then freed from adhering traces of potassium bisdiazooacetate by recrystallisation from water.

For the preparation of the ester, the potassium salt is converted into the silver salt, which after being washed successively with water, absolute alcohol, ether, and finally benzene, is treated with the calcu-

lated quantity of a 25 per cent. solution of methyl iodide in benzene. The mixture is heated on the water-bath for 4 hours, filtered, and freed from benzene at 100° in a vacuum.

The ester so obtained is a thick, syrupy, almost colourless oil, readily soluble in benzene, alcohol, or ether. On standing, it shows signs of becoming crystalline. This compound, together with certain somewhat abnormal derivatives to which it appears to give rise, is still under investigation.

For the preparation of the amide, further purification is unnecessary. One hundred grams of the crude ester are therefore dissolved in 500 c.c. of absolute alcohol and treated with an equal volume of saturated alcoholic ammonia. On standing, the solution slowly deposits the amide as a white, crystalline precipitate consisting of tiny needles, which after recrystallisation from warm water melt at 278° with decomposition. The compound is almost insoluble in the ordinary organic solvents, but dissolves fairly readily in hot water, from which it crystallises in needles or long prisms which show a beautiful play of colours. On analysis, the following results were obtained :

Found C = 28.11 ; H = 3.72 ; N = 48.97.

$C_4H_6O_2N_6$  requires C = 28.32 ; H = 3.53 ; N = 49.40 per cent.

Unlike iminoazoacetamide, this compound gives no precipitate with silver nitrate or even with silver acetate in the presence of ammonium acetate ; copper acetate behaves similarly. Mercuric chloride, on the other hand, produces a pure white precipitate, soluble in boiling water, from which it again separates on cooling. Both hydrochloric and acetic acids dissolve the precipitate readily. Mercurous nitrate gives rise to a white precipitate, soluble in acids, which blackens on boiling. Nessler's reagent produces a white precipitate which turns pale canary-yellow on boiling. These compounds, which N-dihydrotetrazinedicarboxylamide forms with mercury, are exceedingly stable ; even after boiling for half-an-hour with a 25 per cent. solution of caustic soda in the presence of an excess of Nessler's reagent, ammonia could not be detected, although the amide itself is easily saponified on warming with a few drops of dilute caustic soda solution. This, together with the fact that neither copper nor silver salts produce precipitates, seems to indicate that in these mercury salts it is the hydrogen of the  $CONH_2$  group and not that of the imino-group which is displaced, as in the case of iminoazoacetamide. Baryta water in the cold has no effect, but on warming, ammonia is given off and a thick, white precipitate of barium n-dihydrotetrazinedicarboxylate is produced. This salt was identified by the liberation of the acid which melted at 287°, and contained N = 32.30 per cent. [ $C_2H_2N_4(CO_2H)_2$  requires N = 32.56 per cent.].

*Action of Nitrogen Trioxide.*—On treatment with nitrogen trioxide, no bisazoxyacetic acid could be obtained. Triazole is always the principal product of the reaction. Its isolation and identification were conducted precisely as described above under iminoazoacetamide, the yield is 85—90 per cent. of the theoretical. The product melted at 138°. On analysis, the following results was obtained :

Found N = 42·21,  $C_2H_3N_3, HNO_3$  requires N = 42·42 per cent.

*Caustic potash*, either in aqueous or alcoholic solution, readily causes saponification of the amide. One gram of the amide was warmed with a slight excess of a 2 per cent. solution until all odour of ammonia had passed off ; the solution was then evaporated on the water-bath until the potassium salt crystallised out, this, after re-crystallisation from warm water, gave the following result on analysis :

Found N = 22·22 ; K = 31·34.

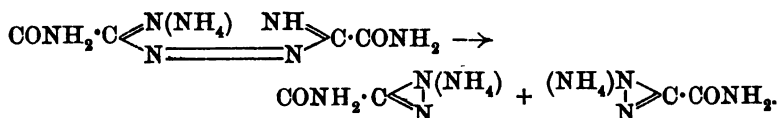
$C_4H_2O_4N_4K_2$  requires N = 22·59 ; K = 31·45 per cent.

#### *Constitution of Iminoazoacetamide.*

From the analysis of its salts and the readiness with which the compound is converted into tetrazine derivatives, it is obviously a bimolecular polymeride of diazoacetamide,  $CHN_2 \cdot CONH_2$ . Its yellow colour indicates the presence of an azo-group. The action of baryta water shows the compound to be the true amide of an acid quite distinct from both bisdiazoacetic acid,  $CO_2H \cdot CH \begin{smallmatrix} N:N \\ N:N \end{smallmatrix} CH \cdot CO_2H$ , and N-dihydrotetrazinedicarboxylic acid,  $CO_2H \cdot C \begin{smallmatrix} NH:N \\ N:NH \end{smallmatrix} C \cdot CO_2H$ .

Further, the preparation and investigation of *n*-dihydrotetrazine-dicarboxylamide has shown that the imino-groups in the tetrazine ring possess properties totally distinct from those of iminoazoacetamide, whilst the production of *isodiazoacetamide* on treatment with ammonia indicates that iminoazoacetamide is a chain compound, and does not contain the stable tetrazine ring at all. In short, the only constitution which explains these apparently contradictory properties is that of iminoazoacetamide,  $NH:C(CONH_2)N:N \cdot C(CONH_2):NH$ .

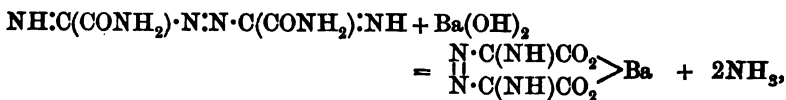
The action of ammonia is rendered clear by the following equation :



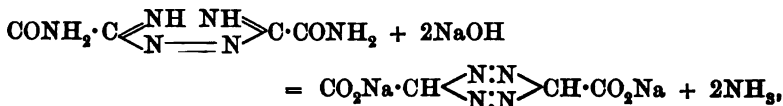
The ease with which derivatives of both C- and N-dihydrotetrazine can be obtained is thus elucidated.



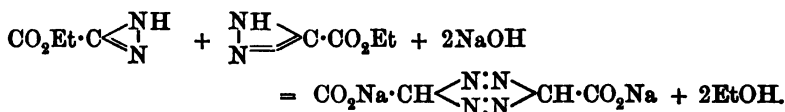
Baryta water gives rise to the corresponding acid,



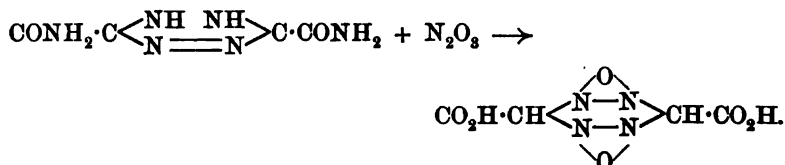
whilst warm caustic soda yields bisdiazooacetic acid,



in a manner precisely analogous to its production from ethyl *iso*-diazooacetate,

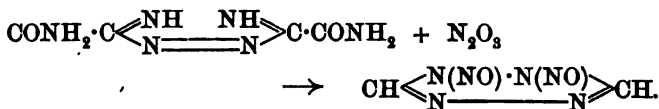


The action of nitrogen trioxide affords additional confirmation of this view, as by its means derivatives of either C- or N-dihydropyrazine can be obtained according to the conditions. The formation of bisazoxyacetic acid is indicated by the following scheme:

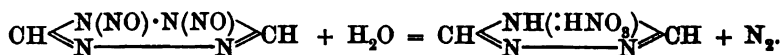


The formation of triazole necessitates the following steps (compare *Trans.*, 1900, 77, 1188, for formation of triazoles from *s*-dinitroso-N-dihydropyrazine and its derivatives):

(a) Formation of *v*-dinitroso-N-dihydropyrazine,



(b) Formation of triazole nitrate,



In conclusion, I wish to express my thanks to the Government Grant Committee of the Royal Society for pecuniary assistance in carrying out this work.

# ANNUAL GENERAL MEETING,

MARCH 26TH, 1902.

Professor J. EMERSON REYNOLDS, M.D., Sc.D., V.P.R.S., President,  
in the Chair.

THE PRESIDENT declared the ballot open for the election of Officers and Council for the ensuing year, Dr. HENRY and Mr. RAMAGE being appointed Scrutators. He then said:—

I have the agreeable duty to-day of congratulating the Fellows on the continued and even increasing prosperity of the Society, as indicated by considerable additions to its list of Fellows, by its consequent gain in the means of promoting its objects, and by the extent and character of the work published during the past year.

The numerical strength of the Society was 2335 on March 28th, 1901. Since that date 163 Fellows have been elected, and 3 have been reinstated by the Council, making a gross total of 2501. Of these, 32 have withdrawn, 25 have been removed for non-payment of two annual subscriptions, and 28 have died.

The actual number of Fellows to date is therefore 2416, the highest number yet reached, and the number of Foreign Members is 32.

The names of those removed for non-payment of subscriptions are:—

E. W. Allsom, W. D. Bohm, C. F. Branson, T. H. Coleman, E. D. Ewen, F. G. Fuller, C. H. Field, W. G. Fraser, A. T. Gailleton, W. H. Grieve, T. C. Hepworth, A. F. Hogg, J. Harger, W. Ince, R. S. Ladell, R. D. Littlefield, D. C. Mackenzie, A. Mackay, F. L. Overend, M. Pearson, S. Smith, A. H. Turton, C. W. Vincent, W. H. Walker, A. Walton.

The following have withdrawn:—

J. M. Arnot, W. H. Barr, F. Belton, H. D. Berridge, M. Cochran, W. Collingridge, J. Craig, H. L. Dampier, M. J. R. Dunstan, G. Evans, H. P. FitzGerald, P. H. Grant, W. H. Greene, H. W. Gough, A. B. Griffiths, J. B. Guyer, H. M. Hastings, E. S. Hayward, A. H. Macdonald, C. J. S. Makin, J. Maudsley, J. McLeod, H. C. Myers, G. A. Parkes, L. G. Patterson, J. C. Quinn, A. Schloesser, C. Thompson, E. A. Wates, J. I. Whimster, B. W. Winder, S. Wood.

The following have died:—

T. H. Aquino, F. J. Beale, J. H. Beckett, Henry Bird, Sir J. H. Gilbert, F.R.S., A. Hartridge, Alexander Hay, Lawrence Hislop, Robert Irvine, David Johnson, N. Leonard, H. G. Madan, William Martindale,

Dr. Ira Moore, Dr. G. Harris Morris, John Paul, Prof. H. von Pechmann, W. B. Randall, W. Shapleigh, Louis Siebold, Prof. Maxwell Simpson, F.R.S., W. T. N. Spivey, W. Terrill, Andrew Thomas, John Thomson, J. L. W. Thudichum, E. A. Warmington, G. F. Wilson, F.R.S.

The most important test of the prosperity of the Society is, however, to be found in the record of its work. In this respect also I have a favourable report to make. Since the last anniversary, 181 communications have been made to the Society. Abstracts of all these have appeared in the *Proceedings*, and 139 have already been published in the *Transactions*. I venture to think that the quality, generally, of the work presented is as high as in any previous year, and clearly indicates the continued enthusiasm and activity of the Fellows.

The *Transactions* for 1901 contain 146 memoirs, occupying 1411 pages; and the volume of the preceding year 127 memoirs occupying 1334 pages.

The volumes for 1901 contain 3754 abstracts of papers, published mainly in Continental journals, occupying 1496 pages, arranged as follows:

## PART I.

	Pages.	No. of Abstracts.
Organic Chemistry .....	784	1530

## PART II.

General and Physical Chemistry .....		403
Inorganic Chemistry .....		376
Mineralogical Chemistry ... ..		169
Physiological Chemistry .....		363
Chemistry of Vegetable Physiology and Agriculture .....		306
Analytical Chemistry.....		607
	712	2224
Total in Parts I. and II. ....	1496	3754

The volume for 1901 contains a Memorial Lecture giving an account of the life-work of Rammelsberg. A set of the Memorial Lectures which had appeared up to the end of 1900 was issued in September last in a separate form.

The use of the Library by the Fellows continues to show their appreciation of it. Eight hundred and eighty books have been borrowed, as against 810 during the corresponding period of last year. A large number of these have been Journals issued by post to Fellows resident in the country, and the Library Committee invite special attention to this development of the Society's usefulness. The additions to the

Library comprise 153 books, 441 volumes of periodicals, and 33 pamphlets as against 95 books, 327 volumes of periodicals, and 30 pamphlets during the corresponding period of last year.

It is desirable that the Society should have in the Library one copy, at least, of every work printed in English on chemical subjects to the end of the 18th century, and I would invite the co-operation of the Fellows in making the Library complete in this direction.

In the preparation of the new Library catalogue, the printing of which has been decided upon, advantage has been taken of the opportunity to construct a new and convenient Card Catalogue, which, it is believed, will materially assist readers in making use of the Library.

It is my privilege to offer, on behalf of the Society, our warm congratulations to Dr. Schunck, to Mr. Lloyd Bullock, and to Dr. Francis, who this year have reached their sixtieth anniversary of admission to the Fellowship of the Society. It gives me pleasure to add that Mr. Buckton, F.R.S., Mr. F. Claudet, and Mr. Darby have reached their jubilee, and to them I would also convey our sincere congratulations.

Last year our illustrious senior Foreign Fellow, M. Berthelot, celebrated the fiftieth anniversary of his first scientific publication, and all countries united in expressing their admiration and respect for the veteran chemist. On behalf of the Society, in company with Dr. Gladstone and Professor Ramsay, I presented a congratulatory address to M. Berthelot at the imposing function which was held in the Sorbonne on November 24th, 1901. That address has already been printed in the *Proceedings*.

During the year, the Society had joined in the celebration of the 450th anniversary of Glasgow University, and in the jubilee of Owens College, Manchester.

Considering the large number of Fellows now in the Society, the mortality is small; nevertheless, this year I regret to say we have lost 21 Fellows. This melancholy list includes the name of Sir Henry Gilbert, Past President of this Society, and one ever devoted to its welfare. His immense work, carried out with Sir John Lawes, laid the scientific foundation of British Agriculture and serves as the model on which all future researches must proceed. The Society was fully represented on the sad occasion when Sir Henry Gilbert was interred, and its representatives laid a wreath on his grave, whilst later on the Council passed a vote of condolence with his mourning relatives. In a short time, I hope, a full obituary notice will be published by one far more competent to undertake it than I am. Dr. Maxwell Simpson is another of those passed away from amongst us full of years, leaving memories of good work well done, especially in synthetic chemistry, and of him and of the other Fellows whose life-work has closed records will also be shortly published.

Considerable discussion has taken place within the Society on the question of altering the day and hour of the Ordinary Meetings, which was raised in the address of my predecessor, Dr. Thorpe, last year. There have been two Extraordinary Meetings on this subject, and the outcome is the experiment now in operation, of trying alternate evening and afternoon Meetings until the end of the present session. Until that experiment has been fairly made, the best course, obviously, is to suspend judgment on the question.

Grants amounting to £250 have been made from the Research Fund in aid of chemical investigations.

This is one of the occasions on which, as I venture to think, it is not only permissible, but desirable, to consider some general question, even of a speculative order, in the light of any new facts discovered in recent years. I therefore propose to discuss as briefly as possible a question of this character, and one which possesses high interest for us, namely, whether the many and important additions to our knowledge of the chemical elements made during the last decade or so have given us any clue to the nature of the relations existing between them.

That the elements are related as a whole is now an axiom, and underlies all modern classification; equally axiomatic is the statement that periodicity can be traced to a large extent between the atomic weights and properties of the elements.

The recognition of this periodic principle by Newlands in 1864, when more fully interpreted by Mendeléeff in 1869, and by Lothar Meyer on somewhat different lines, marked an important advance in science. It served the highly important purposes of correlating a large number of the facts then known, of stimulating research, and of inducing closer scrutiny of the atomic weights. The "periodic law" formulated by Mendeléeff in asserting that "the properties of the elements are periodic functions of their atomic weights" claims an attractive universality, which gained for it much recognition. Mendeléeff's valuable and interesting tabular classification of the elements, arranged in accordance with the "law" and supported by very ingenious and often cogent reasoning, contributed much to its wide acceptance. Later on, the verification of Mendeléeff's brilliant predictions confirmed confidence in the principle. Nevertheless, closer scrutiny revealed difficulties in detail which gradually led to doubts as to the general validity of the "law," and these doubts have been accentuated in recent years by the discovery of the non-valent elements of Rayleigh and Ramsay, for which there seemed at first to be no place in Mendeléeff's classification. It is true that the law neither predicted nor excluded the existence of such elements, and that very



# NOTE TO BINDER.

This diagram is issued to take the place of the one on p. 613 (in the Journal for June), which is to be cancelled and removed.

When the Journal is bound the present diagram should be pasted at the back of the asterisks, and affixed to page 612, so as to face p. 613.

Orthoperiodic Li Be

Macroperiodic

Nodal Helium



doubtful positions have since been assigned to them. More serious difficulties are, however, to be found in the anomalous position given to hydrogen; in the fact that the atomic weight of argon places it between potassium and calcium; that tellurium has a higher atomic weight than iodine, contrary to theory, and in other details which will be specified later on. In consequence, the law is seen to be an empirical rule which, in so far as it properly applies, is of considerable assistance, but is probably only part of a wider generalisation than any we have yet reached.

The difficulties above referred to are masked in the well known table used in illustrating the connection between the atomic weights and the chemical properties of the elements. That this table includes much that is true in reference to the comparative properties of the elements is undoubted, but it has of late been rather used as a convenient system of pigeon holes for elements which are docketed, as it were, with special atomic weights and put away, without much reference to the relations in which they stand to other elements. The fact is there is something beyond the table and beyond the "law" of which we must endeavour to form some conception, if we are to explain existing difficulties. We must therefore get back to the axioms mentioned at the outset, and see whether it is possible to form such a mental picture of the relations subsisting between the elements as shall give us some clue to the nature of those relations, and serve to explain the partial truth of the "periodic law."

The rough outlines of a picture of this kind were, in fact, sketched before 1886,\* but, being rather cumbered by the more rigid notions of valency which then prevailed, the result was not sufficiently clear. Since then, however, important details have been filled in and the discovery of the argon group of elements has given consistence to the whole. The idea underlying the curve which I published in 1886 was that of a vibrating system, based on our knowledge of the properties and relations of the vibrations which physicists term "stationary waves"; but before entering into particulars it is well to define the facts to be kept in view in working out the scheme.

First, and obviously, the atomic weights, on which so much excellent work has been done in recent years, represent the prime group of facts, and those used are the numbers given in the revised table which is printed in the January number of the current volume of the *Berichte*, and are based on the scale of  $O = 16$ . I have indicated these numbers by dots, crosses, or dashes under the scale of equal parts given at the head of the annexed diagram. This is instructive, as it indicates at a glance the more obvious and important numerical relations of the atomic

\* "On a Method of Illustrating the Periodic Law." By J. Emerson Reynolds, *Chem. News*, 1886, 54, 1.



weights or active masses of the elements. As you know, several "laws" have been deduced from the study of these numbers, of which, probably, the best example is Johnstone Stoney's "logarithmic law," but we are not directly concerned with any of these at present.

Secondly, there are the well known relations which may be shortly summed up in the following way. The best defined elements from lithium on, are naturally divisible into sections or "periods," each including seven members; in these periods there is one member, the fourth, which more or less distinctly subdivides it into two parts. Farther, within these periods the first, second, and third members in order of atomic weight are essentially electropositive, and in order of valence; the fifth, sixth, and seventh members are essentially electronegative, and of more variable valence; while the fourth, or unique member, marks a transition, and is generally tetravalent.

Thirdly, we have the very significant fact that, as comparing period with period, and similarly placed elements within the periods, we find the *alternate* members are those which are most closely related in chemical and physical properties. In order to mark this in the diagram the alternate periods are distinguished by different signs—dots for one set, crosses for the other.

Fourthly, in transition from one period to another there is abrupt change of sign, in certain cases, from strongly electropositive to strongly electronegative, as from fluorine to sodium, chlorine to potassium, bromine to caesium, and so on, and it is about such points that we find the atomic weights of the singularly indifferent or neutral elements of the argon group. On the other hand, where there is no such abrupt change of sign from period to period, as from manganese to copper and from molybdenum to silver—that is, in the alternate positions—instead of single non-valent elements, there are groups of three individuals differing little in atomic weights, and all exhibiting high valence comparable with that of the third, fourth, and fifth members of the regular periods. These are the triplets, such as iron, nickel, and cobalt; ruthenium, rhodium, and palladium, &c., which are marked on the scale in the diagram by dashes, and are included in Mendeléeff's unsatisfactory "eighth group."

So far these are matters of fact which are generally admitted, and are stated above independently of any "law" or theory except the atomic theory.

At a very early stage in teaching on the lines of the periodic law, I came to the conclusion that the latter, even when aided by the tabular classification, gave but an imperfect representation of the facts known at the time. One of the clearest deductions from the evidence seemed to be that this peculiar connection between properties and atomic masses must be the outcome of something in the nature of a vibratory

relationship, for only in some such way could all the facts be explained. I therefore sought for some physical phenomena involving periodic change which could help the imagination to form some corresponding picture of the elemental relations, even though no real analogy in the ordinary sense were traceable.

Of all the phenomena suggested for the purpose those vibrations which are known as "stationary waves" seemed the most suitable. They can, as you know, be set up in a light cord fixed at one end and attached at the other to one of the rapidly moving limbs of a large tuning fork, kept in regular vibration by an electro-magnetic arrangement. The motion of the fork is transmitted to the cord with the well known result of establishing a beautiful system of apparently rigid loops and nodes. Each particle of the cord, except at the nodes, travels in a circular path at right angles with the axis of the whole system, the amplitude of the motion being, of course, greatest at the crest of each loop or antinode.

The diagram shows twelve of these small loops which were plotted in the following manner. The atomic weights of the unique, or carbon-silicon, group of elements were marked off alternately at either side of, and at equal distances from, the axial scale; the points were then connected by right lines and the intersection of the scale by each line was taken to mark the node; the loops were then drawn between the nodal points so found. The two loops between 152 and 196 were necessarily obtained by a kind of interpolation, which cannot, however, be much out, as the result is checked by the lead period beyond. The numbers given at the foot of the diagram show the relative lengths of the loops from node to node. These increase up to the sixth loop and then diminish again, just as would happen if the vibrations took place in a medium of unequal density, or the density of the cord was greater nearer the middle of its length than at either end. The axial scale serves to mark off the positions of the atomic masses, which latter are shown by dots and crosses placed on the curve formed by the cord in one phase of vibration. Each dot and cross rapidly rotates in its limited circle round the axis of the whole system and the areas of the circles described increase from the first to the fourth dot and, of course, diminish to the seventh, the direction being the same as that in which the chemical properties of the elements vary. At the nodes there is apparent rest.

Again, as the loops are compared, it is seen that those which are adjacent are in *opposite* phases at any given moment, while the alternate loops are in the *same* phase, just as similarly placed members of alternate periods are found to be most closely allied in properties.

So far as our knowledge extended in 1886, this served as a good

illustration, save in one particular which I shall presently deal with ; but at that time, as I have already said, we were rather hide bound by our conceptions of valency, and the zigzag curve I then published shows this. Even in that form, however, I am glad to know it proved useful in teaching, and that it served, when somewhat modified in form by Sir William Crookes, as a basis on which he has reared his most interesting theory of the genesis of the elements.\*

The unsatisfactory particular to which I referred in the last paragraph was the difficulty in placing the members of the "eighth group." These triplets have atomic weights which place them about the nodal points of the *alternate* periods, but, as you know, they are far from being non-valent. On the contrary, they exhibit properties corresponding to the polyvalent members of the regular periods. It is true that their compounds are, generally speaking, easily reduced, and the elements themselves by no means active in the free state, but the fact remains that they all exhibit high valency. The idea suggested by these and other considerations was that they are members of another series of elements harmonically related to the first series, somewhat as shown on the diagram by the larger loops. From that point of view they are "interperiodic," but in a new sense ; and in one, moreover, which is consistent with their appearance only about the *alternate* nodes of the regular periods. Whether or not these large vibrations should be represented as taking place at exactly half the rate of the smaller ones, was a subject often discussed with my valued colleague, the late Professor G. F. Fitzgerald, but we agreed that it is sufficient for the general purpose in view to take the simplest relationship between the two sets of vibrations as shown in the diagram. The difficulty about the hypothesis was that we had then no evidence of the existence of any other elements which could be supposed to belong to the special series, and the picture remained incomplete until the discovery of argon and its allies supplied the necessary links. It had already been foreseen that any other elements of the slow moving triplet series which might exist would probably exhibit much feebler chemical activity than those of any of the smaller periods, but the existence of non-valent elements was not anticipated.

Once the latter were discovered, however, they were seen to be just of the kind required to complete the picture. Their atomic weights placed them at or very near to each of the nodes which is *apparently* common to both vibrating systems, and their non-valence in contrast with the antinodal triplets sufficiently accounted for the absence of intermediate elements of the same series.

\* Address to the Chemical Section of the British Association at the Birmingham meeting in 1886, and *Trans.*, 1888, 53, 487.

I must now invite your attention to another matter of interest which bears on the disputed question of the position of hydrogen in relation to the rest of the elements.

I have already described the means adopted for deducing the nodal points of the minor periods from the atomic weights of the members of the carbon-silicon group. But between carbon (12) and zero, the symmetry of the particular loop necessarily guided its continuation and fixed its node at 4 on the scale, or slightly in advance of the number which was subsequently found to represent the atomic weight of helium. At the time, it was difficult to understand this exceptional shortening of the loops, but on making the experiment with a cord some 4 metres in length thrown into "stationary waves," I found that when partially stopped with the finger so as to compel the formation of a node at some 4 units from the vibrator, the nearest loops were found to be shortened relatively and, approximately, in the proportions indicated on the diagram, a result which naturally increased confidence in the value of the picture as a whole. In thus definitely fixing the node at 4 units of the scale, the curve between that point and the vibrator necessarily assumed the form shown on the diagram which represents the "cut-off" end of the loop. Now, hydrogen must find its place here at 1.008 of the scale; therefore, from our point of view, hydrogen seems to be the *last* member of a period rather than (as supposed by Mendeléeff) the first of a seven-member period, of which six are still unknown. On general grounds also, the facts now known support this view to which we have been led as to the position of hydrogen, though I am inclined to think that the *role* of that element in nature is far more important than that of a typical halogen; but I shall return to this point shortly.

Having now worked in most of the details of the picture, we can next consider its general effect. Before doing so, however, it is convenient to designate as :

*Orthoperiodic*.—The members of the twelve minor periods.

*Macroperiodic*.—The triplets represented about the antinodes of the greater periods.

*Nodal*.—The elements of the argon type.

Broadly speaking, this scheme represents the atomic masses as forming a dual vibrating system, the two parts of which exhibit apparently simple harmonic relations. Whether or not these relations are quite so simple as they appear to be, there is no doubt that the system as a whole also gives some evidence of still wider periodicity, as the lengths of the middle loops are somewhat greater than those on either side.

From our point of view, hydrogen, so far from being limited in its analogies as the end element of a period, seems rather to be the

elemental material which is a type of *both* atomic series, and therefore cannot be claimed as the first term of any single group of elements.

Of the *nodal* elements, helium marks the node common to the two vibrating systems, and the strong contrasts between fluorine and sodium account for the presence of the nodal neon at 20, instead of the macroperiodic triplet, which analogy would otherwise lead us to expect to find about this point. The next element of the nodal class, argon, brings us at once to a case which is at variance with the periodic law.

No difficulty would arise if argon had an atomic weight just below that of potassium, but Ramsay does not admit a lower value than 39.9, and this we are bound to accept. The result is that the neutral argon is placed between the two strongly positive elements, potassium and calcium, which differ from one another only in degree. In the cases of helium, neon, krypton, and xenon, the elements occur in neutral positions between strongly contrasted substances, positive and negative. Argon is, therefore, quite exceptional, and breaks the order required by the "law." From our present point of view, we have, however, the choice of two hypotheses. One is that argon is not strictly nodal, and is to be placed a little beyond the common node on the major loop, so that its position between potassium and calcium is apparent rather than real, but this implies the possession of very feeble chemical properties. The other was suggested by Prof. Fitzgerald, namely, that the nodes of the minor and major loops do not quite coincide, and that of the latter is at 39.9.

It is probable that at least two other nodal elements remain to be discovered. One of these should have an atomic weight about 174 and the other near 218.

Turning now to the *Macroperiodic* elements, I have already stated the reason for thinking that no triplets are likely to exist with atomic weights round 20.

The iron, palladium and platinum sets of triplets, forming Mendeléeff's "eighth" group, fall naturally into their places on the major vibrations. Their neighbourhood disturbs the symmetry of the minor periods, and more especially do they appear to influence the properties of the elements nearest in atomic weight so far as they are known. On the other hand, as Mendeléeff ingeniously seeks to show, the adjacent elements retain in some degree their "group" characters, hence he justifies the classification of chromium with oxygen and sulphur, and of manganese with the halogens. Nevertheless, he assumes that each set of triplets, together with the elements near in atomic weight, form a single "long period"; but, in view of the preceding contention, this really implies the admission of periods within periods. It appears to me that the nature of the relations of the triplets to the periods

between which they occur is more consistently represented as harmonic in character.

I need scarcely say that our knowledge of the elements with atomic weights between 140 and 195, that is, the "rare earths," is still very unsatisfactory; but the didymium elements—praseodymium, neodymium, and samarium—possess some characters which seem to give ground for supposing that they may be the macroperiodic triplets wanting between 140 and 150, and they are shown in the diagram in this position. The two first-named elements each give two oxides, unlike most of the other rare earths; all three elements afford coloured salts; their solutions exhibiting characteristic absorption spectra; and the oxides have been found by du Bois and Otto Liebknecht\* to show high paramagnetic susceptibility, only second to that of the members of the iron triplet. I venture to make the suggestion that they belong to the macroperiods with all reserve, as our knowledge of these substances is still limited.†

The next point of interest to be considered principally affects the *Orthoperiodic* series. I refer to the question of the relative positions of iodine and tellurium. According to the rigid form of the periodic law, the atomic weight of tellurium should be just below that of iodine, as selenium is below bromine, sulphur below chlorine, and oxygen below fluorine. All the best determinations of the atomic weight of tellurium, however, seem to leave no doubt that it is higher than that of iodine by nearly a unit. There is here direct conflict between the "law" and the fact, in which the latter must prevail. From our present point of view the explanation is simple enough.

Iodine is the element which has the highest atomic weight of any known number of the "halogen" group. One of the most characteristic properties of members of the group is their power of combining with hydrogen to form the acids of the type  $HX$ . Now hydrofluoric, hydrochloric, and hydrobromic acids are exothermic compounds, the heat of formation of hydrobromic acid being the lowest. Hydriodic acid, on the other hand, is an endothermic compound, as energy must be supplied in its formation. In this particular, therefore, iodine has almost lost the important group characteristic, while its power of forming fairly stable compounds with oxygen is much greater than that of its lower homologues. But iodine departs still further from the halogen rôle in its power of forming with phenyl, and other similar radicles, basic substances of the hydroxylamine type—the iodonium compounds discovered by Hartmann and Victor Meyer in 1894. In

\* *Ber.*, 1899, 32, 3344. Compare Stefan Meyer, *Monatsh.*, 1900, 20, 269.

† *Note added May 17th.*—It appears from *Nature* of May 15th that Brauner has just published a paper with the Russian Chemical Society adopting a similar view as to the positions of the didymium elements.

the compound  $\text{IPh}_3$ , derived from  $\text{IPh}_2\cdot\text{OH}$ , trivalent iodine must be recognised simulating nitrogen, so far as the capacity of the latter is concerned for holding unoxidised radicles and affording basic products, notwithstanding the fact that iodine does not form a simple hydrogen compound of the same order as ammonia. In this respect, then, iodine draws near to antimony, so that, whatever the conditions were which prevailed at "the birth of the elements," it would seem that the increase in mass of the somewhat indifferent iodine grouping was checked by the pull of its more positive neighbour, while tellurium was free to gain instead.

With the rare elements which seem to form only sesquioxides, little can be done at present. So far as definite atomic weights have been assigned to them they are marked on the diagram, but with all reserve. There are obviously several elements of the higher periods still unknown.

We have no certain knowledge of elements of higher atomic weight than bismuth, save thorium and uranium; but the radioactive substances radium, polonium, and actinium, if elements in the usual sense, probably have high atomic weights also, and may ultimately be found to fill some of the gaps in this neighbourhood.

Substances of the radium class are known to constantly give off cathodic radiations which can perform definite chemical work on a sensitive plate, and, according to Professor J. J. Thomson, they must have emitted similar radiations for millions of years. Such a steady distribution of energy must be balanced by a supply *ab extra*, just as the moving particles of the cord receive theirs from the vibrator; but we have not as yet any clue to the source or sources from whence radium and its allies draw their supplies. All that we definitely know is that the active substances—whether simple or compound—are comparatively massive molecules, which serve for the collection of energy and its distribution partly, at least, in radiant forms. This rather suggests the idea that the less massive atoms of the other elements may also act in varying degrees as energy transformers into different orders of chemical activity.

Dr. GLADSTONE, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed in the *Transactions*.

Dr. THORPE, C.B., F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having returned thanks,

Prof. TILDEN, F.R.S., the Treasurer, in giving an account of the Balance Sheet which he laid before the Society, duly audited, said :—

The receipts had been :—By admission fees and subscriptions, £4532 ; by sale of Journal and advertisements, £835 11s. 2d. ; and by dividends on invested capital, £476 12s. 6d. The total receipts from all sources amounted to £5884 1s. 8d. The expenses had been :—On account of the Journal, £3233 0s. 2d. ; on account of the Proceedings, £20 1s. 5d. ; on account of the Library Catalogue, £42 14s. 4d. ; on account of the Library, £429 15s. 5d. ; House expenses, £239 19s. 1d. ; the total expenditure being £4913 10s. 6d.

The TREASURER, in concluding, proposed a vote of thanks to the auditors, which was acknowledged by Mr. CHAPMAN.

Prof. H. B. DIXON, F.R.S., proposed a vote of thanks to the Treasurer, Secretaries, and Council.

Dr. HEWITT seconded the motion, which was unanimously adopted. Prof. MELDOLA, F.R.S., responded.

The Scrutators having presented their report to the President, he declared that the following had been duly elected :—

*President* : J. Emerson Reynolds, Sc.D., M.D., V.P.R.S.

*Vice-Presidents who have filled the office of President* : Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S. ; H. E. Armstrong, Ph.D., LL.D., F.R.S. ; A. Crum Brown, D.Sc., LL.D., F.R.S. ; Sir W. Crookes, F.R.S. ; J. Dewar, M.A., LL.D., F.R.S. ; J. H. Gladstone, Ph.D., D.Sc., F.R.S. ; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S. ; H. Müller, Ph.D., LL.D., F.R.S. ; W. Odling, M.B., F.R.S. ; W. H. Perkin, Ph.D., LL.D., F.R.S. ; Sir H. E. Roscoe, LL.D., F.R.S. ; W. J. Russell, Ph.D., F.R.S. ; T. E. Thorpe, C.B., LL.D., F.R.S. ; A. W. Williamson, LL.D., F.R.S.

*Vice-Presidents* : E. Divers, M.D., D.Sc., F.R.S. ; P. F. Frankland, LL.D., F.R.S. ; H. McLeod, F.R.S. ; R. Meldola, F.R.S. ; H. A. Miers, D.Sc., F.R.S. ; T. Stevenson, M.D.

*Secretaries* : W. R. Dunstan, M.A., F.R.S. ; A. Scott, M.A., D.Sc., F.R.S.

*Foreign Secretary* : W. Ramsay, LL.D., F.R.S.

*Treasurer* : W. A. Tilden, D.Sc., F.R.S.

*Other Members of Council* : H. B. Baker, M.A. ; F. D. Chattaway, Ph.D., D.Sc. ; F. Clowes, D.Sc. ; J. J. Dobbie, M.A., D.Sc. ; A. E. Dixon, M.D. ; M. O. Forster, Ph.D., D.Sc. ; A. Harden, M.Sc., Ph.D. ; J. Lewkowitsch, Ph.D. ; J. E. Marsh, M.A. ; S. U. Pickering, M.A., F.R.S. ; J. A. Voelcker, Ph.D. ; J. Walker, D.Sc., F.R.S.



## THE TREASURER IN ACCOUNT WITH THE CHEMICAL

DR.

	£	s.	d.	£	s.	d.
Balance at Bank, March 24th, 1900	1818	12	7			
„ In hands of Treasurer	0	1	8			
						1913 13 10
<b>Receipts by Life Compositions, Admission Fees and Subscriptions from March 23rd, 1901, to March 22nd, 1902:—</b>						
Life Compositions—3 at £30, 1 Bal. at £28, 1 at £20, 1 at £12, 1 at £10, 1 Bal. at £8	168	0	0			
163 Admission Fees	652	0	0			
4 Subscriptions for 1899 „ £2	8	0	0			
1 Subscription for 1900 „ £1	1	0	0			
181 Subscriptions for „ „ £2	262	0	0			
6 „ „ „ 1901 „ £1	6	0	0			
722 „ „ „ „ „ £2	1444	0	0			
5 „ „ „ 1902 „ £1	5	0	0			
998 „ „ „ „ „ £2	1986	0	0			
						4532 0 0
Sale of Journals	689	13	8			
„ Proceedings	12	18	0			
„ General Index	22	4	8			
„ Sale of Memorial Lectures	27	10	6			
Proceeds of Advertisements in Journal	83	4	9			
						835 11 8
Subscription from the Society of Chemical Industry to June, 1901...	8	8	0			
„ „ „ Public Analysts to January 1st, 1902	11	11	0			
„ „ „ Physical Society to January 1st, 1902	19	19	0			
						89 18 0
Repayment of Income Tax	22	14	0			
Year's Dividends on £6,780 Metropolitan Board of Works $\frac{1}{2}$ per cent. Stock	222	6	2			
„ „ £1,060 London and North-Western Railway Debenture Stock	29	14	7			
„ „ £1,520 14s. 3d. Cardiff Corporation Stock	42	19	4			
„ „ £1,400 India $\frac{1}{2}$ per cent. Stock	33	0	9			
„ „ £2,358 Midland $\frac{1}{2}$ per cent. Preference	55	13	8			
„ „ £2,400 Bristol $\frac{1}{2}$ per cent. Debenture	56	10	0			
Interest on Bank Deposit	13	15	0			
						476 12 6

<i>Assets.</i>	<i>Estimated Value.</i>		
	<i>£</i>	<i>s.</i>	<i>d.</i>
March 23rd, 1901.			
Balance at Bank (Current Account) .....	2034	0	9
"    "    (on Deposit) .....	1000	0	0
"    "    in hands of Treasurer .....		4	8
£6,780 Metropolitan Board of Works $\frac{3}{4}$ per cent. Stock	7201	2	0
£1,060 London and North-Western Railway Debenture Stock .....	1065	15	0
£1,580 14s. 3d. Cardiff Corporation 3 per cent. Stock...	1466	16	0
£2,380 Midland Railway $\frac{3}{4}$ per cent. Preference .....	1851	0	7
£2,400 Bristol Corporation $\frac{3}{4}$ per cent. Debenture Stock	1992	0	0
£1,400 India $\frac{3}{4}$ per cent. Stock .....	1197	0	0
	£17807	18	7

SOCIETY, FROM MARCH 23RD, 1901, TO MARCH 22ND, 1902.

Cr.

*Expenses on Account of the Journal and Proceedings.*

	£	s.	d.	£	s.	d.	£	s.	d.
Salary of Editor .....	250	0	0						
" Sub-Editor .....	200	0	0						
" Indexer .....	80	0	0						
Editorial Postages .....	13	16	5						
Abstractors' Fees.....	359	19	2						
Printing of Journal.....	1668	15	0						
Printing of Advertisements .....	29	16	8						
Printing Wrappers .....	184	5	0						
Distribution of Journal by Printers .....	884	15	6						
" Society .....	15	6	5						
Authors' Copies.....	98	1	0						
Illustrations for Journal .....	3	5	0						
				2233	0	2			
Printing of Proceedings.....	156	0	1						
Distribution of Proceedings.....	50	1	4						
				206	1	5			
Publishers' Commission.....	73	4	9						
Advertising Agents' Commission .....	12	0	9						
				85	14	6			

*Expenses on Account of Collective Index 1898—1902.*

Salaries .....	65	11	1			
Petty expenses .....	1	17	11			
Index Slips .....	5	9	0			
				72	18	0

*Expenses on Account of the Library Catalogue.*

Salaries .....	30	10	0			
Petty expenses .....	0	14	4			
Case for Catalogue .....	11	10	0			
				42	14	4

*Expenses on Account of the Library.*

Salary of Library Assistant .....	49	13	0			
Books and Periodicals .....	311	6	11			
Binding .....	76	15	6			
				429	15	5

*House Expenses.*

Providing Refreshments .....	22	0	10			
Lighting the Building..... (Gas, £20 5s. 2d.; Electric Light, £30 18s. 1d.).....	41	8	8			
Heating the Building (Coals) .....	90	19	6			
Cleaning .....	15	0	0			
Repairs .....	41	5	2			
Petty House Expenses .....	26	8	1			
House Porter's Wages .....	65	0	0			
" Uniform .....	5	19	0			
Annual Fee to Gate Porter .....	2	2	0			
Inhabited House Duty .....	0	6	8			
				289	19	1

Salary of Assistant Secretary.....	200	0	0			
Pension to Mr. Hall .....	180	0	0			
Miscellaneous Printing .....	78	14	4			
Stationery .....	14	1	8			
Addresses to M. Berthelot and the Owens College .....	3	12	0			
Indexing for International Catalogue .....	80	6	4			
Expenses on account of Anniversary Dinner .....	37	7	6			
Legal Charges .....	16	6	0			
Show-case for Medals and Framing Portraits, &c. ....	13	4	0			
Memorial Lectures, Binding of .....	18	7	3			
Bank Charges .....	0	9	9			
Treasurer's Petty Cash Disbursements .....	0	2	0			
" Assistant.....	10	0	0			
Postage Account: Office and Secretarial Postages, £9 4s. 7d.; Postal Cards and Stamped Envelopes (Clay), £29 2s. 2d.; Embossed Stamps, £12 10s. ....	50	16	9			
				4913	10	6

Transferred to Deposit Account.....	250	0	0			
Balance at Bank .....	2031	0	9			
" in hands of Treasurer .....	0	4	3			

**£7197 15 6**

Audited with vouchers and found correct. } ALF. C. CHAPMAN.  
J. T. HEWITT.  
L. T. THORNE,

22nd March, 1902,



## OBITUARY NOTICES.

SIR JOSEPH HENRY GILBERT, Ph.D., M.A., LL.D., Sc.D., F.R.S.,  
born August 1st, 1817, died December 23rd, 1901.

ON May 18th, 1841, when the Chemical Society was barely three months old (it having been founded on February 23rd of that year), there was elected to the Fellowship a young man of twenty-four, who was destined to play an important part in the history of the Society and in that of the progress of chemical science and investigation, and whose name, in conjunction with that of his fellow-worker and patron, Sir John Bennet Lawes, was to be for ever associated with the benefits which chemistry has conferred on the industry of agriculture. This young man was Joseph Henry Gilbert, born at Hull of parents well-known in the literary world, and himself lately returned from Giessen, where he had been studying under Liebig. His earlier years had been impaired, and his future career threatened, by an accident which deprived him of the use of one eye, but his subsequent record forms a striking instance of triumph over physical disability. He had worked at Glasgow University under Prof. Thomas Thomson, Stenhouse being there, as also at Giessen, his fellow student. At Giessen, whither he was attracted by Liebig's fame, he had not only Stenhouse, but also Playfair, as companions, and here took his degree of Ph.D. Returning to England, he worked at University College, London, and became assistant to Dr. A. T. Thomson, meeting here also J. B. Lawes, with whom he was afterwards to be so closely identified. It was at this time that, as stated, he became a Fellow of the Chemical Society, and so was almost one of its original members.

Forty-one years later (1882) he was elected to the Presidential Chair, serving in this capacity during the session 1882-3, and sixteen years later he formed one of the group of six Past-Presidents whose fifty years' continuous membership of the Society was celebrated by the remarkable and unique gathering of November 11th, 1898, when a banquet was given in honour of the distinguished veterans in science—Gilbert, Frankland, Odling, Abel, Williamson, and Gladstone. Of this group, Gilbert was the senior, Playfair, who would have formed the seventh member and the only original member of the Society among the seven—for other original members were then living—having passed away only a few months previously.

In reviewing Gilbert's work one cannot do better than recall some of the remarks which were made at the notable banquet referred to, as they apply with special force to Gilbert's character and aims. The then President, Prof. Dewar, spoke of the guests thus honoured as

"men whose one idea has been, with steady aim and vigilant eye, to labour on with that sole incentive of scientific work, the triumphant hope of making an advance. These men have laboured for half a century in our interests, and they have added enormously to our knowledge of the science . . . . We are still able to go back to a man, who sits on my right hand (Gilbert), who worked in the laboratory of Thomas Thomson, who has seen Dalton and the beginning of the atomic theory." Then, addressing himself to Gilbert, he said, "The work of Gilbert, as we know, was early differentiated into that most complex and mysterious study, the study of organic life. For the last fifty years he has devoted his attention to the physiology of plant life in every phase of its development. With a skill that has been unprecedented, he has recorded from year to year the variations in the growth of every kind of nutritious plant. He has examined into the meteorological conditions, the variations of climate, of soil, and of mineral agents, of drainage, and of every conceivable thing affecting the production and development of plant growth. These memoirs are admitted throughout the world to be unique in their importance. Wherever the chemist or the physiologist, the statistician or the economist has to deal with these problems, he must turn to the results of the Rothamsted experiments in order to understand the position of the science of our time. These results will be for ever memorable; they are unique and characteristic of the indomitable perseverance and energy of our venerated President, Sir Henry Gilbert."

These words most aptly describe the life-work of Gilbert, and when it is remembered that for another 3 years after this he laboured on unremittingly and died positively "in harness," some idea can be formed of the devotion of Gilbert to the pursuit of the science he has so largely enriched.

Gilbert's first contribution to the Chemical Society's Memoirs was the translation of a paper by Redtenbacher and Liebig on "The Atomic Weight of Carbon"—this was previous to his formal admission to the Society. But it was in 1843 that the important step was taken by him which shaped his future career, for it was then that he was invited by Lawes, who had been his fellow student at University College, London, to assist him in the agricultural investigations which he had just begun on coming into possession of his country property at Rothamsted, Herts. From that time began the unbroken collaboration which, for its duration, intimacy, and results on agriculture, has had no parallel.

The name "Rothamsted," from being merely that of a country gentleman's seat, has come to designate a storehouse of knowledge, and a centre from which the efforts of two distinguished men, each working on his own line but combining their powers in the setting-out

of their joint conclusions, have been put forward for the elucidation of nature's secrets and the benefit of the great industry of agriculture.

It is hard, and it would be undesirable, to attempt to separate the work of two men so closely associated, for "Lawes and Gilbert" is the fitting expression for this unique collaboration. Still, it may not be amiss to point out how great was, in the case of both men, the influence of the scientific method in investigating the problems of practical agriculture and in framing the conclusions to be drawn. Gilbert was remarkable for the complete conscientiousness of his work, the extreme care and patience which he displayed, the scrupulousness with which he verified his results by frequent repetition, the pertinacity with which he maintained the continuation of the experiments when once set on foot and defended the conclusions drawn from them, and for his untiring energy, his life-long devotion to the work in the thorough conviction—which we can now share—that what he was engaged in would remain as a monument and an example for the future. No one could be brought into contact with Gilbert without feeling that it was for Rothamsted that he lived, his one aim was not his own aggrandisement (for there was little of this in his case), but the making of Rothamsted a centre of usefulness and the home of agricultural research. Few men have there been who have set before them such single-minded purposes as Gilbert, his own position, his own advancement, it can be truly said of him, were put aside for higher considerations, and what honours and distinctions were accorded to him sprang from the initiative of an appreciative public outside, and were none of his seeking.

To every worker who cared to apply to him, Gilbert was ever ready to give help, and sincere is the gratitude which the younger generation of agricultural chemists feel towards him for what he has done for them, and for the way in which he endeavoured to elucidate any point in the Rothamsted experiments.

Gilbert was, in fact, the exponent of the Rothamsted work and the one to familiarise its results and lessons to the scientific world. In this capacity he frequently read or wrote papers for the Chemical Society, the Royal Agricultural Society, and other bodies, and in pursuit of the same idea he would attend the meetings of the British Association, or visit the Continent, or make journeys to Canada or the United States.

None of those who were privileged to know him well will ever forget his demonstrations in the Rothamsted laboratory, his expositions in the field, and the infinite care that he took to make everything clear and to emphasise it finally by reference to that vast series of tables with which all students of Rothamsted have become familiar.

Not even increase of years seemed to dim the energy or activity, still less the enthusiasm, of Gilbert, and it was not until after the death of Sir John Lawes in August, 1900, that he showed any signs of failing health. Even then he could not be persuaded to put his work aside or take a needed rest, but continued, as before, to send in his regular reports to the Lawes Trust Committee, and to plan out work for future development.

In disposition, Gilbert was most friendly and amiable. Everyone had a good word to say for him. Jealousy of anyone else seemed to have no place in his nature, and desire of personal gain was an element foreign to his character. His devotion to work was shared in and ably aided by his wife—the present Lady Gilbert—who survives him, and to whose unremitting care is largely due that he was so long spared to continue his labours.

To detail Gilbert's work would be to write the account of the Rothamsted experiments—a task beyond the limits of the present notice—and it is only necessary to recall the fact that it dates from the time of the inception of the “mineral theory” of Liebig—which made way for the “nitrogen theory” of Rothamsted—to the comparatively recent questions of soil organisms and assimilation of atmospheric nitrogen by plants.

Gilbert was made a Fellow of the Royal Society in 1860, and in 1867 he, with Lawes, received a Royal medal of that Society. Many other distinctions from learned societies, public bodies, and universities followed the prolific work emanating from Rothamsted. Oxford University made him Sibthorpe Professor of Rural Economy in 1884, the Albert Gold Medal of the Society of Arts was awarded him, and the conclusion of 50 years of Lawes and Gilbert's joint labours was marked by a presentation to him on July 29, 1893, and the inscription of his name, together with that of Lawes, on a granite monolith erected in front of the Rothamsted Laboratory. As a fitting sequence, Gilbert was, to universal satisfaction, given, by her late Majesty Queen Victoria, the honour of knighthood.

He died at his own house, at Harpenden, which adjoins the scene of his labours, and now he rests in the village churchyard there beside his life-long associate, Lawes. Many may well envy the encomium on Gilbert which the *Spectator* expressed when it said of him “He achieved the rare distinction of gaining a world-wide reputation without being known to the man-in-the-street.”

J. A. V.

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HENRY GEORGE MADAN, who died on the 22nd of December, 1901, was born on September 6th, 1838, and after being educated at a private school near Bath and at Marlborough College gained a classical

exhibition at Corpus Christi College, Oxford, in 1857. He obtained a second class in Moderations and a first class in Natural Science, and in 1862 was elected to a Fellowship at Queen's College, which he held for the remainder of his life. From 1863 to 1869 he was demonstrator in chemistry in the University. In 1869 appeared the first edition of the well-known *Exercises in Practical Chemistry*, written by Mr. A. G. Vernon Harcourt and himself. In the same year, he was appointed First Science Master at Eton College. He held this post for twenty years, and, though not an inspiring lecturer or one able to obtain a mastery over unwilling boys, he was an admirable teacher for those who desired to learn; by them his labours as a schoolmaster will always be appreciated and remembered with real gratitude.

Among his published works are to be mentioned a new edition of *Wilson's Inorganic Chemistry* (1871), *Lessons in Elementary Dynamics* (1886), *An Elementary Treatise on Heat* (1889), *Tables of Quantitative Analysis* (1881), and several papers and notes on optical experiments and their demonstration. His name is not associated with much original work, but the observations on the remarkable potassium chlorate crystals afterwards investigated by Stokes are noteworthy. Towards the close of his life he devoted much attention to optical research and to the British Association bibliography of spectroscopy.

A few years before his death, he was crippled by an accident which deprived him of his right arm and disabled one leg, and doubtless laid the seeds of his fatal illness. To a man of his extraordinary bodily activity who devoted himself, even in advanced years, to rowing as an exercise and to dextrous mechanical work as a pastime, the loss must have been heartbreaking; but it only gave him the opportunity of displaying his unyielding and strenuous character; he had always steeled himself against the exhibition of feeling; and with indomitable energy he returned as far as possible to his scientific work.

Mr. Madan possessed a keen and rigid intellect; he was an able experimentalist and a fine mechanician, and used to say that he never employed a machine which he could not make for himself. He was also an excellent scholar; in this connection it will be remembered that he suggested the Homeric names, Deimos and Phobos, for the satellites of Mars.

His scientific apparatus, much of which was made by himself, he distributed before his death, partly to his College, and partly to the Mineralogical Department of the University Museum as a gift to one of his old pupils.

H. A. M.

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Mr. W. B. RANDALL, of Southampton, who died on March 14th, aged 81, was one of the oldest of our Fellows, having been elected as an Associate in April 1843. Originally an apothecary in the old sense of the word, he finally adopted pharmacy as his profession.



Mr. Randall was a private pupil of Mr. R. Warrington, the first Secretary of the Chemical Society, and studied Chemistry at University College under Thomas Graham, taking the Silver Medal in the session of 1843. Mr. Randall was a J.P. for Southampton, and had held office on the City Council and as Chairman of the School Board.

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SAVILLE SHAW was born at Ardwick, Manchester, on December 22nd, 1864. He received his early education at the Manchester Commercial School, and while at school displayed that keen interest in experimental science which he retained through life, and which, no doubt, led to his pursuing his education at the Owens College, where he became a student in 1880. During the period he was at Owens College, Shaw devoted himself mainly to the study of chemistry under Sir Henry E. Roscoe, and after completing his course spent a year in the "Doctor's" private laboratory. It was at this time that he conducted the investigations on pentathionic acid and the pentathionates, the results of which were embodied in a paper published in the Transactions of this Society for the year 1883.

In January, 1884, Saville Shaw, who had just entered on his twentieth year, came to Newcastle as assistant in the Chemical Department of the Durham College of Science, with which institution he was associated until his untimely death, a period of upwards of seventeen years. At first with the duties of this post those of lecture assistant were combined, in the discharge of which Shaw displayed great care and ingenuity, and a resourcefulness which the writer of this notice has had occasion repeatedly to admire and thankfully to appreciate. Relinquishing this work after a time, he became lecturer in chemistry, devoting himself to the teaching in the laboratory and the lecture room, in both of which his quiet manner, his knowledge, and his keen appreciation of the difficulties of the student contributed to make him popular as a teacher. Nor was this alone the opinion of the College students, for under the auspices of the County Councils of Northumberland and Durham he gave several courses of lectures in various parts of these two counties, and by schoolmasters and miners alike his lectures were highly valued and appreciated.

When, in 1890, the College in enlarging its sphere of work added a Department of Metallurgy, Mr. Shaw, who had always shown a special leaning to inorganic chemistry and the chemistry of the metals, was elected to take charge of this department, and in this capacity commenced an investigation on the micro-structure of alloys. Of the results of this investigation he has only published a short note, which appeared in *Nature*, August 11th, 1898, accompanied by reproductions of two photographs of sections, which show well his admirable skill in this class of work. Amongst his effects have been found a large

number of photographs and sections and also the notes relating thereto, which Mr. Stead has undertaken to edit for publication.

Despite the arduous duties of his post and a by no means robust constitution, Shaw was not unmindful of the fact that in an industrial community there are many problems the scientific investigation of which may serve to advance knowledge and help at the same time to the proper understanding by the layman of the advantages of a scientific training. Thus, he not only lent valuable assistance to the writer in an investigation of the cause of the explosion of an air-receiver at one of the neighbouring collieries, but also was one of the most regular attendants at the meetings of the Flameless Explosives Committee formed by the North of England Institute of Mining and Mechanical Engineers, and in the conduct of the numerous experiments of that committee gave invaluable aid and contributed to the report a special section dealing with "Gases and Gaseous Mixtures."

Since Shaw took a great interest in the literature of his own country, he had a facile pen and a keen and somewhat caustic wit, to which he occasionally gave liberty in verses which were much enjoyed by a small circle of friends.

For some years he acted as Hon. Sec. and Treasurer to the Newcastle Section of the Society of Chemical Industry, for which body he laboured most successfully, his organising power and ability finding expression in the great success of the general meeting of that society which was held in Newcastle in 1899. To mark their sense of appreciation of his work, the members of this section have subscribed to found a medal, which is to be awarded as a prize to students in chemistry or metallurgy, so that his memory may be always associated with the science to which he was so devoted.

His unassuming modesty and kindly nature endeared him to his colleagues, to whom and to his relations his sudden death on November 5th, 1900, came as a great shock.

In 1896, the University of Durham, in recognition of his work in connection with the College of Science and the extension lectures in the county, conferred on him the degree of M.Sc. P. P. B.

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MAXWELL SIMPSON, who died in London on February 26th last, was a son of Mr. Thomas Simpson, of Beech Hill, co. Armagh, Ireland, and was the youngest of a family of nine. He was born on March 15th, 1815, and thus nearly completed his eighty-seventh year. He was educated at a private school in Newry, which was well known at the time, kept by Dr. Henderson, and from this school he passed into Trinity College, Dublin.

In his early boyhood he was much in the company of the brilliant and witty Charles James Lever, the novelist and physician. Susceptible as he was throughout his life to personal influences, the conversa-

tion of Lever, which often turned on physiological problems, led the young Simpson to look to the profession of medicine as his future career. But with this directing impulse towards science there was also a natural restlessness, a seeking after new ideas, new impressions, which may well have been intensified by the example of the author of "Charles O'Malley," himself a wanderer, who died in a distant land. Thus, after taking his A.B. degree, he did not then proceed to the M.B., but travelled to London, from which place he made several journeys to Paris.

During one of these visits to Paris he attended the lectures of Dumas. This was a great event in his life. Within the charm of this great investigator and teacher, of the personality so well remembered by many of us, the Irish student found what he had dreamt of, what he had longed and sought for. He found satisfaction for that restless discontentedness with a conventional career which had led him to wander from home, that healthy discontent to which the world is indebted for so many great men. He built for himself in his imagination an ultimate object of life, an ideal; he saw the possibility of molecular structures of never-ending wonder and beauty, and he pledged himself to endeavour to realise them. To this ideal he remained fervently true throughout his life. Maxwell Simpson was a man of wide culture and never-failing humour, and a personality as kind as it was true; but no one really knew him who did not know of his ideal. Like the knight in Dürer's picture, he rode on; all other things which most men prize—wealth and worldly recognition—he brushed aside; he had one single object only, his ideal, which meant the pursuit of chemistry.

On his return to London he decided to go through a preliminary training in chemistry, and for that purpose entered Graham's laboratory in University College, where he remained two years. After this, in 1845, he settled in Dublin and married a daughter of Mr. Samuel Martin, of Langthorne, co. Down. Mrs. Simpson entered with an enthusiasm which never relaxed into her husband's ideal and made it her own. Much of his success was due to her womanly tact and counsel. In 1847 he became lecturer in chemistry at the Park Street Medical School, called later the Ledwich School of Medicine, and in order to hold this position he took his M.B. degree at Dublin University. He retained this lectureship until 1857.

In 1851 he longed once more for that atmosphere of scientific research which was found then, as now, in its best development in the universities of the Continent. He obtained leave of absence from the Medical School and went with his wife and family to Germany, where he remained three years. The happy scientific and social intercourse of those years always remained fresh in the memories of Dr. and Mrs. Simpson, and in after years nothing pleased them better than to relate

to their friends their pleasant experiences of "plain living and high thinking" in the university towns on the Neckar and the Lahn. Like other foreign students who are privileged to enjoy both German living and German thinking, Maxwell Simpson became a missionary of the culture and industry of the Germans to his native land.

After his training in Graham's laboratory he was prepared to begin original inquiries, and in the laboratory of Bunsen in Heidelberg, and of Kolbe in Marburg, he made good progress. In these laboratories he had among his fellow workers and friends many who have since become well known in the annals of science. His first published paper emanating from Heidelberg was on improved methods of organic analysis: "Ueber neue Methoden zur Bestimmung des Stickstoffs in organischen und unorganischen Verbindungen" (*Annalen*, 1855, 95, 63). These methods are especially applicable to compounds which burn with difficulty, and a full account of them will be found in Fresenius's "Quantitative Analysis" and in Roscoe and Schorlemmer's "Treatise on Chemistry."

Maxwell Simpson returned in 1854 to his medical classes in Dublin, but they seem to have interfered too much with the pursuit of his ideal, for in 1857 he resigned the lectureship and proceeded with his family once more to the Continent. This time it was Wurtz, in Paris, who, by his discovery of the glycols, attracted him, as he attracted other students, to his laboratory. Here he worked for upwards of two years enjoying the same friendly intercourse among French chemists that he had experienced before among the Germans across the Rhine. His inquiries were directed to the elucidation of the theory of polyhydric alcohols. At this period he published "Note concernant l'action du Brôme sur l'Iodide d'Aldéhyde" (*Compt. rend.*, 1858, 56, 467); "On the Action of Acids on Glycol," two papers (*Proc. Roy. Soc.*, 1859, 9, 725; 1860, 10, 114); "Action du Chlorure d'Acétyle sur l'Aldéhyde" (*Compt. rend.*, 1858, 47, 874); "Sur une Base nouvelle obtenue par l'Action de l'Ammoniaque sur le Tribromure d'Allyle" (*Compt. rend.*, 1858, 46, 785).

Returning once more to Dublin in 1860, he fitted up a laboratory in his house in Wellington Road where, for seven years under the most difficult conditions, he pursued his inquiries, and where his greatest successes were achieved. In the back kitchen of this house he obtained for the first time synthetically succinic and other di- and tri-basic acids. That alkyl cyanides on hydrolysis yield monobasic acids was known; but he was the first to apply the reaction to the cyanides of the dyad and triad radicles, obtaining di- and tri-basic acids. Thus, he prepared succinic acid from ethylene dicyanide, pyrotartaric acid from propylene dicyanide, tricarballic acid from tricyanopropane, and also many hydroxy-acids from corresponding cyanides. The following contributions were the result of work done in Wellington Road: "On a Com-

pound of Dibromallylammonia and Chloride of Mercury" (*Phil. Mag.*, 1859, [iv], 17, 194); "On Cyanide of Ethylene and Succinic Acid" (*Proc. Roy. Soc.*, 1860, 10, 574); "On the Synthesis of Succinic and Pyrotartaric Acids" (*Phil. Trans.*, 1860, 61); "On the Action of Chloride of Iodine on Iodide of Ethylene and Propylene Gas" (*Proc. Roy. Soc.*, 1862, 11, 590); "On the Synthesis of Tribasic Acids" (*Proc. Roy. Soc.*, 1863, 12, 236; this Journ., 1865, 18, 331); "On the Direct Transformation of Iodide of Allyle into Iodide of Propyle" (*Proc. Roy. Soc.*, 1863, 12, 533); "On the Acids Derivable from the Cyanides of the Oxy-Radicles of the Di- and Tri-atomic Alcohols" (*Proc. Roy. Soc.*, 1864, 13, 44); "On the Action of Chloride of Iodine upon Organic Bodies" (*Proc. Roy. Soc.*, 1864, 13, 540); "On the Formation of Di-iodacetone" (*Laboratory*, 1867, 1, 79); "On the Direct Transformation of Chloride of Ethylidene into Glycol" (*Phil. Mag.*, 1868, [iv], 35, 282); "On some New Derivatives of Acetone" (*Proc. Roy. Soc.*, 1868, 16, 364).

In 1867 he again visited Paris and continued his researches in Wurtz's laboratory. These inquiries resulted in two memoirs, the one "On the Formation of Succinic Acid from Chloride of Ethylidene" (*Report Brit. Assoc.*, 1867, 42), and the other in conjunction with A. Gautier, "Sur une Combinaison Directe d'Aldéhyde et d'Acide Cyanhydrique" (*Compt. rend.*, 1867, 65, 414). He then resided in London for a few years, when he acted as Examiner at Woolwich, Coopers Hill, and for the Indian Civil Service. He examined also in Materia Medica for the Queen's University in Ireland.

Maxwell Simpson, at the age of 57, received his first important appointment, and thereby became entitled to a regular professional income for the first time. On the death of Dr. John Blyth in 1872, he was appointed Professor in Queen's College, Cork. He took to the Cork College the prestige of a scientific inquirer, well known in the laboratories of England, France, and Germany. He held the chair for nearly twenty years, when he retired in 1891. The behaviour of iodine chloride in organic reactions had always interested him, and this and other subjects attracted his attention while in Cork. He published the following papers: "On the Bromiodides" (*Proc. Roy. Soc.*, 1873, 22, 51); "On the Determination of Urea by Means of Hypobromite of Soda," in conjunction with Mr. C. O'Keeffe (this Journal, 1877, i, 538); "Chemical Notes" (*Proc. Roy. Soc.*, 1878, 27, 118); "On the Formation of Chlor-Iodide and Brom-Iodide of Ethylidene" (*Proc. Roy. Soc.*, 1878, 27, 424). After retirement from the Cork chair in 1891 he resided in London.

The discoveries of Maxwell Simpson without doubt place him among the great chemists who laid the foundations of organic chemistry in the last century. But it may be that still greater than his actual achievements was his life-long devotion to the prosecution of

science, to the ideal he formed for himself under the influence of Dumas.

Maxwell Simpson became a Fellow of the Chemical Society in 1857, served as a Member of the Council 1864—1870, and Vice-President, 1872—1874; Fellow of the Royal Society, 1862; Honorary Fellow of the King's and Queen's College of Physicians of Ireland, 1865; Senator of the Queen's University in Ireland, 1873—1882; President of the Chemical Section of the British Association, 1878; Fellow of the Royal University of Ireland, 1882—1891. He received the degrees of M.D., 1864, and LL.D., 1878, from Dublin University, and D.Sc., 1882, from the Queen's University, *honoris causa*. A. S.

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WILLIAM THOMAS NEWTON SPIVEY.—On October 9th, 1901, a serious accident occurred in the University Chemical Laboratory, Cambridge, which a fortnight later led to the death of Mr. W. T. N. Spivey, and robbed the University of one of the most promising and popular members of its chemical school, adding one more name to the roll of those who have lost their lives in the pursuit of science.

Mr. Spivey was born on the last day of the year 1868, and received his early education at Elmfield College, York, where he at once gave evidence of the all round thoroughness which characterised his later work. In 1883, while still at Elmfield, he gained distinction in almost all the subjects of the Cambridge Local Examination, taking the first place in mathematics and chemistry, and thus winning a scholarship at the High School, Newcastle-under-Lyme. From 1883 to 1887 he worked at Newcastle, chiefly at science and mathematics, and while there, passed the London Matriculation Examination, taking the first place on the Honours List, and thus gaining the Exhibition. About the same time, he was elected to a sub-sizarship at Trinity College, Cambridge, for science and mathematics, and came into residence in October, 1887.

His career as an undergraduate was marked by success, the result of diligence and enthusiasm in his work in the laboratories. In 1889, he was placed in the first class in Part I of the Natural Science Tripos. In the same year he was elected a Scholar of his college, and in 1891 he gained a First Class in Part II of the Natural Science Tripos, with chemistry as his chief, and physics as his second, subject, and proceeded to his B.A. degree. He continued to reside in Cambridge, giving much of his time to teaching both as a junior demonstrator in the University Chemical Laboratory, and as a private tutor, and during these years proceeded to his M.A. degree at Cambridge, and his London B.Sc.

In 1896, he left Cambridge to take the post of Science Master at Epsom College, where he at once showed himself to be a successful teacher. Before the end of the year, however, he returned to Cambridge, being invited by Professor Dewar to become Jacksonian

Demonstrator in the University, which post he continued to hold until the day of his death.

As a lecturer, he at once attained great popularity, and all his courses of lectures were largely attended. He was especially successful in his lectures on advanced organic chemistry, in which subject his very wide reading and his extraordinarily methodical mind enabled him to arrange the vast amount of information in his lectures in an orderly, logical, and systematic manner which was of the greatest benefit to his pupils. As a demonstrator, his kindly, genial manner, and his earnestness and enthusiasm for his subject, marked him out as the man to whom the student in difficulty always turned for help, with the certainty of receiving the most careful and courteous explanation, however trivial or however wide the question might be.

His great popularity among the students was shown by the success which attended his effort to reorganise the Students' Chemical Club, of which he was secretary at the time of his death, and which he left in a thoroughly flourishing condition.

With so large a proportion of his time ungrudgingly given up to teaching, Mr. Spivey's contributions to chemical research were not so numerous as they might have been had he used for his own work the time he gave so willingly to helping others.

The formation of closed carbon chains by condensations starting from acetylene tetrabromide first claimed his attention, but he was unfortunately anticipated in the publication of his results. He then undertook with two of his colleagues in the University Chemical Laboratory an investigation on the active principle of Indian hemp, which, together with a number of terpenes and other compounds occurring in hemp, formed the subject of two papers in the Transactions of the Society. Concurrently with this work he was engaged in the synthesis of various terpene derivatives, but again had the misfortune to be anticipated.

It was while he was preparing material for the synthesis of cannabinolactone, a derivative of cannabinol, the narcotic principle of Indian hemp, that he met with the sad accident which ultimately caused his death. A flask containing a considerable quantity of carbon disulphide, which he had been using as a diluent in Étard's reaction for preparing aromatic aldehydes, accidentally broke in his hand after the reaction had been completed. Some of the disulphide saturated his clothes, the rest vaporised, and the explosive mixture of vapour and air became ignited. The explosion caused several wounds but the most serious injuries were the burns due to the ignition of the disulphide with which his clothes were saturated. All appeared to be going well with him for a week after the accident, when pneumonia, which so frequently follows severe burns, supervened and caused his death after a second week's painful illness.

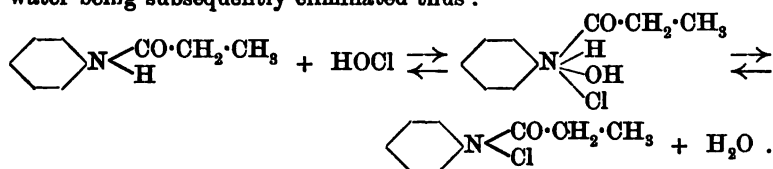
T. B. W.

# LXV.—*Nitrogen Chlorides containing the Propionyl Group.*

By F. D. CHATAWAY.

ANILIDES containing the propionyl group have been comparatively little studied, and their derivatives are entirely unknown. In the course of an investigation of the effect produced upon the properties of substituted nitrogen chlorides and bromides by a change of acyl group, a number of such substances have been prepared.

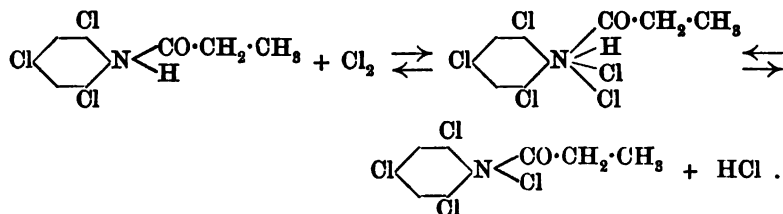
Aniline and the chloroanilines, when they are heated with propionic anhydride or in the case of symmetrical tri-derivatives with propionyl chloride, readily yield propionanilides. These resemble closely the corresponding acetyl compounds, but differ from them in the prevailing habit of the crystals, and in a more ready solubility in organic solvents. All the propionanilides, on treatment with hypochlorous acid, yield substituted nitrogen chlorides. Hypochlorites are probably first formed, the nitrogen developing its higher valency and water being subsequently eliminated thus :



The action appears to be a reversible one, for on placing a nitrogen chloride in water the opposite change takes place to a small extent until a position of equilibrium is reached.

These nitrogen chlorides show all the characteristic reactions of the group, a noticeable feature of such reactions being the invariable replacement of the halogen by hydrogen.

Some of these changes are reversible, the following equation, for example, expresses what takes place when chlorine is passed into a solution of an anilide, or hydrogen chloride into a solution of the corresponding nitrogen chloride :



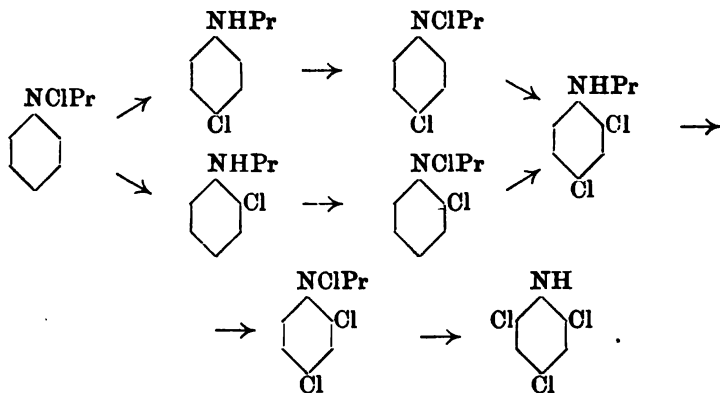


The direction in which action takes place depends on the relative masses of the various substances in the system. In presence of salts of weaker acids, such as propionic or acetic, which remove the hydrogen chloride as fast as it is formed, the nitrogen chloride is produced, whilst if excess of hydrochloric acid be added, or the chlorine withdrawn as it is liberated, the anilide is re-formed.

When hydrogen is attached to the phenyl nucleus either in the para- or the ortho-position, these nitrogen chlorides readily undergo isomeric change.

When an unsubstituted phenyl group is present, the chlorine atom attached to the nitrogen and a hydrogen atom, either in a para- or an ortho-position change places, and a chloropropionanilide results.

When either of these positions is occupied by halogen, exchange takes place into the one still occupied by hydrogen, whilst when both the para- and one ortho-position have been taken up, the halogen passes, although somewhat less readily, into the remaining unfilled ortho-position. No transference of halogen from the nitrogen to a meta-position has been observed. The following scheme shows the direction of transformation :



These intramolecular rearrangements take place on heating and especially readily under the influence of chlorine or reagents, such as hydrogen chloride, which can cause the liberation of chlorine.

When nitrogen chlorides containing phenyl groups with an ortho- or para-position unoccupied by halogen take part in the group reactions previously referred to, the primary action often plays quite a subordinate part owing to the rapid transformation, induced by the reagent or by some product of the change, destroying the nitrogen chloride before it can enter into reaction. The behaviour of propionyl phenyl nitrogen chloride with hydrochloric acid or with alcohol may be given as an example.

These isomeric changes, which follow exactly the course of direct substitution, strengthen the view that in the chlorination and bromination of anilines and anilides the halogen becomes first attached to the nitrogen, and then, during the periodic motions of the molecule, passes into the more stable configuration where it is attached to the ring. In the presence of an amino-group or of an acyl imino-group, the other atoms or groups present exert a comparatively inappreciable influence.

#### EXPERIMENTAL.

##### *Propionyl Phenyl Nitrogen Chloride*, $C_6H_5 \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$ .

This compound is best prepared by adding a large excess of a solution of sodium hypochlorite containing potassium bicarbonate to an alcoholic solution of propionanilide, both cooled to zero. The nitrogen chloride slowly separates in small, hard plates. It is very readily soluble in chloroform or benzene, and easily in warm petroleum of low boiling point. It crystallises from the latter solvent in colourless, transparent, glistening plates, apparently rectangular with domed ends, and melts at  $77^\circ$ :

0.2054 liberated  $I = 22.3$  c.c.  $N/10$  iodine.\*  $Cl$  as  $N \cdot Cl = 19.24$ .

$C_6H_{10}O \cdot NCl$  requires  $Cl$  as  $N \cdot Cl = 19.31$  per cent.

On being heated rapidly above its melting point, this compound undergoes transformation suddenly at about  $180-190^\circ$  with considerable development of heat to a reddish, slightly impure, mixture of *p*- and *o*-chloropropionanilide. This transformation is also brought about by heating the nitrogen chloride under a little water, or by passing into its solution in any solvent a few bubbles of hydrogen chloride. In the latter case, the isomeric change is very rapid, and the solution boils violently from the heat developed. It is slowly and quantitatively transformed with a very slight development of colour when dissolved in chloroform to which a few drops of propionic acid have been added and the solution allowed to stand for some days. About 90 per cent. of the *p*- and 10 per cent of the *o*-chloropropionanilide are produced.

##### *p*-Chloropropionanilide, $C_6H_4Cl \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$ .

This can be easily obtained by once crystallising from alcohol the transformation product of propionyl phenyl nitrogen chloride. On account of the inevitable slight waste in purification and the cost of

\* All the nitrogen chlorides and bromides described in this paper were analysed in the same way. A weighed quantity was dissolved in dilute acetic acid, excess of potassium iodide added, and the liberated iodine estimated by a decinormal solution of sodium thiosulphate.

propionic anhydride, it is more economical to prepare it from *p*-chloro-aniline. This base, when mixed with the equivalent quantity of propionic anhydride, readily reacts with considerable development of heat, and the operation is completed by heating for an hour to 120° in an oil-bath, the solid product being recrystallised first from alcohol and finally from chloroform. It is sparingly soluble in petroleum of low boiling point, but readily so in acetic acid, alcohol, or chloroform. From the latter solvent, it separates in small, glistening, four-sided, apparently rhombic plates, and melts at 141°:

0.2005 gave 0.1562 AgCl. Cl = 19.26.

$C_9H_{10}ONCl$  requires Cl = 19.31 per cent.

*Propionyl p-Chlorophenyl Nitrogen Chloride*,  $C_6H_4Cl \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$ .

This compound was prepared and purified by the method just described. In solubility and general properties, it closely resembles the phenyl compound. It crystallises from petroleum of low boiling point in glistening, colourless, apparently rectangular plates with domed edges, and melts at 55°. When heated above this temperature, it begins to darken in colour at about 150° and at about 210° undergoes transformation into 2:4-dichloropropionanilide with considerable development of heat. When treated as described on p. 639, this transformation takes place quantitatively:

0.2069 liberated I = 19 c.c. *N*/10 iodine. Cl as  $N \cdot Cl$  = 16.28.

$C_9H_9OCl \cdot NCl$  requires Cl as  $N \cdot Cl$  = 16.26 per cent.

*Propionyl p-Chlorophenyl Nitrogen Bromide*,  $C_6H_4Cl \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$ .

This, like all the nitrogen bromides described in this paper, was prepared by shaking the corresponding propionanilide dissolved in chloroform for about an hour with a solution of hypobromous acid\* containing a little potassium bicarbonate. The chloroform solution was well washed with water, and finally with very dilute alkali to remove any free bromine, dried, and the solvent evaporated off on a water-bath in a current of dry air. When the chloroform was completely removed, the yellow oil thus obtained solidified on cooling to a pale yellow solid, which was best purified by recrystallisation from petroleum of low boiling point. This, like the nitrogen bromides described later, is a yellow, well crystallised solid very readily soluble in benzene or chloroform, and moderately so in petroleum.

Propionyl *p*-chlorophenyl nitrogen bromide crystallises in groups of long, glistening, bright yellow, transparent rhombic prisms, apparently four-sided with domed ends, and melts at 71°:

\* Made by shaking mercuric oxide suspended in water with bromine.

0.3564 liberated I = 27.1 c.c. *N*/10 iodine. Br as :N·Br = 30.4.

$C_9H_9OCl:NBr$  requires Br as :N·Br = 30.45 per cent.

It is readily transformed into 4-chloro-2-bromopropionanilide when its solution in chloroform containing a few drops of acetic acid is allowed to stand for some days in a sealed tube.

*o*-Chloropropionanilide,  $C_6H_4Cl \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$ .

This substance is best prepared by heating *o*-chloroaniline with propionic anhydride. Considerable heat is evolved on mixing these substances, and the action is complete after an hour's heating at 120°. The product is very readily soluble in ordinary solvents, and crystallises well from petroleum (b. p. 80—100°) in groups of colourless, glistening, needle-like plates melting at 91°:

0.1831 gave 0.1421 AgCl. Cl = 19.19.

$C_9H_9ONCl$  requires Cl = 19.31 per cent.

*Propionyl o*-Chlorophenyl Nitrogen Chloride,  $C_6H_4Cl \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$ .

This compound crystallises from light petroleum in groups of glistening, colourless, transparent rhombic plates with domed edges and melts at 57°:

0.1969 liberated I = 17.9 c.c. *N*/10 iodine. Cl as :N·Cl = 16.11.

$C_9H_9OCl:NCl$  requires Cl as :N·Cl = 16.26 per cent.

It is more stable than the corresponding *p*-chloro-derivative, but is transformed quantitatively into 2:4-dichloropropionanilide if heated at 150° in a sealed tube with a few drops of propionic acid. When heated above its melting point, it decomposes at about 220°, but the product is dark in colour and contains only a little of the isomeric anilide.

*Propionyl o*-Chlorophenyl Nitrogen Bromide,  $C_6H_4Cl \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$ .

This nitrogen bromide crystallises from petroleum of low boiling point in elongated, four-sided rhombic prisms, often 1—2 cm. in length, of a very pale yellow colour, and melts at 106°. It is much less soluble in all solvents than the other nitrogen halogen compounds described in this paper:

0.3625 liberated I = 27.5 c.c. *N*/10 iodine. Br as :N·Br = 30.33.

$C_9H_9OCl:NBr$  requires Br as :N·Br = 30.45 per cent.

When slowly heated in a sealed tube with a few drops of propionic acid at about 140°, it is transformed into 4-chloro-6-bromopropionanilide.

2:4-Dichloropropionanilide,  $C_6H_3Cl_2 \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$ .

This compound can be prepared by the direct chlorination of propionanilide dissolved in acetic acid, but is most easily obtained by heating 2:4-dichloroaniline with the equivalent quantity of propionic anhydride at  $160^\circ$  for 3 hours. It crystallises from alcohol in long, colourless, flattened prisms and melts at  $121^\circ$ . It is easily soluble in chloroform and crystallises well from this solvent in long, silky needles :

0.1484 yielded 0.1946 AgCl. Cl = 32.42.

$C_9H_9ONCl_2$  requires Cl = 32.52 per cent.

Propionyl 2:4-Dichlorophenyl Nitrogen Chloride,  
 $C_6H_3Cl_2 \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$ .

This is most easily prepared by dissolving 2:4-dichloropropionanilide in a little cold glacial acetic acid, and slowly pouring into this an excess of a strong solution of bleaching powder. A pale yellow oily liquid is thrown down. This is extracted with petroleum of low boiling point, washed well with water and a dilute solution of potassium bicarbonate, and dried. On allowing the solvent to evaporate in a vacuum, the nitrogen chloride separates in glistening, colourless, transparent, flat rhombic plates, apparently rectangular with domed edges,\* and melts at  $64^\circ$ . It is extremely soluble in chloroform, but cannot be crystallised from this solvent, as a mere trace of it prevents solidification.

This compound can also be easily prepared by dissolving propionanilide, *p*-chloropropionanilide, or 2:4-dichloropropionanilide in cold glacial acetic acid containing an excess of sodium acetate, and passing chlorine into the cooled solution until it is no longer absorbed. On adding water to the product and extracting with petroleum as above, a theoretical yield is obtained :

0.3204 liberated I = 25.4 c.c. *N*/10 iodine. Cl as  $:N \cdot Cl = 14.05$ .

$C_9H_9OCl_2 \cdot NCl$  requires Cl as  $:N \cdot Cl = 14.04$  per cent.

Propionyl 2:4-dichlorophenyl nitrogen chloride is very stable, and can be heated at  $100^\circ$  in a sealed tube for a long time without change. It undergoes transformation, however, into 2:4:6-trichloropropionanilide on heating for a short time at  $150^\circ$  in a sealed tube with a

\* Most of the hydrogen halogen derivatives containing the propionyl group crystallise from petroleum in modifications of this form and are thus distinguished from the acetyl derivatives, which, as a rule, separate from this solvent in prisms with domed ends.

little propionic acid. When heated alone above  $100^{\circ}$ , it slowly darkens in colour, and at about  $220$ — $230^{\circ}$  decomposes, giving off a little chlorine, and leaving a dark coloured, tarry mass. When heated with water, it is slowly hydrolysed, 2:4-dichloropropionanilide and hypochlorous acid being formed. When it is treated with cold hydrochloric acid, chlorine is rapidly evolved, and 2:4-dichloropropionanilide regenerated.

*Propionyl 2:4-Dichlorophenyl Nitrogen Bromide,*  
 $C_6H_3Cl_2 \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$ .

This crystallises from petroleum at low boiling point in glistening, transparent rhombs of a very pale yellow colour, and melts at  $66^{\circ}$ :

0.4374 liberated  $I = 29.5$  c.c.  $N/10$  iodine. Br as  $:N \cdot Br = 26.96$ .

$C_6H_5OCl_2 \cdot NBr$  requires Br as  $:N \cdot Br = 26.92$  per cent.

It is readily transformed into 2:4-dichloro-6-bromopropionanilide when heated for a short time at  $140^{\circ}$  in a sealed tube with a few drops of propionic acid. Heated alone in an open tube, it begins to darken in colour at about  $110^{\circ}$ , and is transformed with some decomposition at  $160$ — $170^{\circ}$ .

*2:4:6-Trichloropropionanilide,*  $C_6H_2Cl_3 \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$ .

This was obtained by heating together 2:4:6-trichloroaniline with a slight excess of propionyl chloride until hydrogen chloride was no longer evolved, the temperature being finally raised to about  $180^{\circ}$ . It was recrystallised from alcohol, in which it is readily soluble, and from which it separates in long, colourless, flattened prisms, melting at  $161^{\circ}$ :

0.1473 gave 0.2504  $AgCl$ .  $Cl = 42.03$ .

$C_6H_5ONCl_2$  requires  $Cl = 42.12$  per cent.

*Propionyl 2:4:6-Trichlorophenyl Nitrogen Chloride,*  
 $C_6H_2Cl_3 \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$ .

This substance is best prepared by adding an excess of a solution of bleaching powder to a solution of the anilide in glacial acetic acid. It separates at first as a yellow oil which after some time solidifies. It crystallises well from petroleum of low boiling point in clusters of small, elongated plates which have a pearly appearance when pressed together; these melt at  $80^{\circ}$ . When heated above its melting point, it decomposes at about  $230^{\circ}$ :

0.1618 liberated  $I = 11.3$  c.c.  $N/10$  iodine.  $Cl$  as  $:N \cdot Cl = 12.38$ .

$C_6H_5OCl_2 \cdot NCl$  requires  $Cl$  as  $:N \cdot Cl = 12.35$  per cent.

*Propionyl 2 : 4 : 6-Trichlorophenyl Nitrogen Bromide,*  
 $C_6H_2Cl_3 \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3.$

This compound crystallises from petroleum (b. p. 80—100°) in bright yellow, rhombic plates and melts at 106°. When heated above its melting point, it decomposes about 180°, giving off bromine :

0.2660 liberated I = 16 c.c. *N*/10 iodine. Br as :N·Br = 24.05.

$C_6H_7OCl_3 \cdot NBr$  requires Br as :N·Br = 24.12 per cent.

It may be noted that the nitrogen bromides derived from chloropropionanilide and from 2 : 4 : 6-trichloropropionanilide, which have a symmetrical structure, are of a bright yellow colour, whilst those derived from *o*-chloropropionanilide and 2 : 4-dichloropropionanilide, which have an unsymmetrical structure, are very pale yellow in colour.

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## LXVI.—*Dimercurammonium Nitrite and its Haloid Derivatives.*

By PRAFULLA CHANDRA RAY, D.Sc. (Edin.).

SINCE the publication in the Proceedings (1901, 17, 96) of a note on the subject of the present paper, I have, after fuller consideration of the facts, arrived at somewhat different conclusions from those I had then come to; when, therefore, any statement in this paper differs from what is found in that note, it is to be taken as expressing my later view of the matter. The experimental results remain unaltered.

It has already been pointed out by me (*Zeit. anorg. Chem.*, 1896, 12, 365; *Trans.*, 1897, 71, 337) that mercurous nitrite is partly decomposed by water into mercury and a solution of both mercurous and mercuric nitrites, and that when this solution has been prepared by triturating the salt with cold water, about 22 per cent. of the salt dissolves without decomposition.\* The proportions of the two nitrites

\* In my paper on mercurous nitrite in the *Annalen* (1901, 316, 250), it is stated (p. 252) that much the greater part of this salt dissolves in water unchanged; but that is a clerical error, made in translating. Another error in that paper is the reference (p. 250) to the notice of this salt published by Divers and Haga in the *Transactions*. The reference to the statement of these chemists about mercurous

in solution may therefore be formulated by  $4\text{Hg}(\text{NO}_2)_2 + (\text{HgNO}_2)_2$ . The addition of sodium chloride precipitates the mercury of the mercurous salt and leaves in solution mercuric and sodium nitrites, no doubt as one or more double salts, similar to that described recently by Rosenheim (*Zeit. anorg. Chem.*, 1901, 28, 171). It is probable that the solution of the two mercury nitrites contains them as double salts also, mercuric-mercurous nitrites, firstly, because neither of the two is obtainable in solution by itself; secondly, because mercurous nitrite dissolving in a solution of sodium or potassium nitrite is wholly decomposed into metal and mercuric nitrite combined with the alkali nitrite, and, thirdly, because, as pointed out in earlier papers, the solution of the mixed nitrites is neutral to litmus, whereas even mercuric chloride is acid in absence of an alkali chloride. On the other hand, however, it should be mentioned that during the spontaneous evaporation of this solution, hydrated mercurous nitrite crystallises out (*Trans.*, 1897, 71, 340). The non-acidity of these mercuric-mercurous nitrite and mercuric-sodium nitrite solutions, as well as their stability on dilution, distinguishes them from that of either of the mercury nitrates, and other differences are to be found in their behaviour with urea and with sodium sulphate, neither of which precipitates them (*Trans.*, 1897, 71, 1103).

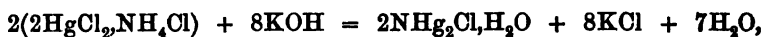
Feeling that the formation of stable and neutral double salts of mercuric nitrite gives support to the view that nitrites have a constitution allied to that of haloid salts, as distinct from that of oxylic salts such as the nitrates, it occurred to me that further insight into the matter might be gained by a study of the action of ammonia on mercuric-sodium nitrite. Ammonia yields with the mercuric-sodium nitrite solution an insoluble compound having the composition expressed by the formula  $\text{NHg}_2\text{NO}_2$ , together with a little less than half a mol. of water, of which it is partly deprived when exposed in a desiccator; it is slightly decomposed in the steam-oven. Since mercuric nitrate, similarly treated, gives also a somewhat hydrated precipitate,  $\text{NHg}_2\text{NO}_3$ , which, according to Pesci, becomes anhydrous when thoroughly washed with boiling water, a treatment hardly possible in the case of the nitrite, the composition of the ammoniated nitrite fails to throw the expected light on the constitution of nitrites.

The ammoniated mercuric nitrite and its haloid derivatives have, however, a special interest in the support they afford to the dimercur-ammonium theory propounded by Rammelsberg in 1888 (*J. pr. Chem.*, [ii], 38, 558), and since extended to all ammoniated mercury compound. The composition of the ammoniated mercuric nitrite is also erroneously given in the footnote to my paper on this salt in the *Transactions* (1897, 71, 387). In both cases it should have been to *Proc.*, 1886, 2, 250, and *Trans.*, 1887, 51, 49.



pounds by Pesci (*Gazzetta*, 1890, 19, 509, and 20, 485). The anhydrous nitrate is known (Rammelsberg, Pesci), and the anhydrous bromide (Pesci), as well as the impure anhydrous chloride (Wehl, Rammelsberg), but in the rest of the ammoniated mercury compounds the dimercurammonium salt assumed to be present is so either in combination with water, or with ammonium salt, or with mercury salt. The double salts, however, behave in every respect as such (Rammelsberg, Pesci), familiar instances of which are the two 'white precipitates,'  $\text{NHg}_2\text{Cl}, \text{NH}_4\text{Cl}$  and  $\text{NHg}_2\text{Cl}, 3\text{NH}_4\text{Cl}$ . But hydrated dimercurammonium salts—Millon's, or oxydimercurammonium, salts—do not yield water until the salt itself decomposes. This water is, however, readily displaceable by ammonium salts (Pesci, André, and others), whilst its fixity to heat before decomposition of the salt may be no more than what is seen in the like behaviour of hydrated aluminium chloride, hydrated magnesium chloride, and many other salts. K. A. Hofmann and Marburg, it is true, deny the existence of dimercurammonium salts (*Annalen*, 1899, 305, 191), but Pesci's reply to them (*Zeit. anorg. Chem.*, 1899, 21, 361) is an experimental refutation of most of their objections.

Now, the ammoniated nitrite, having at most only half the hydration necessary to constitute the oxydimercurammonium nitrite, must be at least half dimercurammonium salt. Not only is this the case, but it has yielded me, in a way to be described presently, a dimercurammonium chloride and a bromide, each also with only half the hydration demanded by the oxydimercurammonium constitution. Finally, this half mol. of water can seemingly be displaced by a half mol. of either mercuric bromide or chloride. The half-hydrated dimercurammonium chloride had already been obtained by André in 1889 (*Compt. rend.*, 108, 1164), although unknown to me when I was examining it. André's method of getting it is perfectly definite, and consists in treating mercuric chloride in dilute solution with ammonia equivalent to one-fourth of its chlorine in presence of potassium hydroxide equivalent to the rest, thus ensuring the non-formation of any ammonium chloride. My success was gained in essentially the same way, for I had present only just enough ammonia to supply the nitrogen of the dimercurammonium. Having prepared from the ammoniated nitrite the new double mercuric-ammonium salts,  $2\text{HgCl}_2, \text{NH}_4\text{Cl}$  and  $2\text{HgBr}_2, \text{NH}_4\text{Br}$ , I treated them each with potassium hydroxide, and in this way secured the conditions I have mentioned. The interaction occurs according to the equation:



as I proved by finding always four-fifths of the chlorine in the mother liquor. By using a little less potash, I have sometimes succeeded in

getting the salt  $2\text{NHg}_2\text{Br.HgBr}_2$ , and, in an impure state,  $2\text{NHg}_2\text{Cl.HgCl}_2$ , which salts, it is evident, can only be written down as dimercurammonium compounds.

## EXPERIMENTAL.

*Dimercurammonium Nitrite.*—In order to prepare this salt, mercurous nitrite is acted on by water so as to obtain a solution of mercurio-mercurous nitrite, which is then changed to one of mercuric-sodium nitrite by careful addition of just enough sodium chloride. As in the case of silver nitrate and sodium chloride, the end point is hard to hit off, and with every care a minute but unimportant quantity of either mercurous salt or of chloride must be left in solution. Another and better way of preparing mercuric-sodium nitrite solution is to dissolve mercurous nitrite in a concentrated solution of sodium nitrite, when half the mercury separates as metal; but with this I only became well acquainted too late for use in the work of this paper. Solutions of mercuric-sodium nitrite can also be prepared by adding either mercuric (Rosenheim) or mercurous nitrate to sodium nitrite solution, but these, of course, contain sodium nitrate, which, for this investigation, would be an undesirable, although probably inactive, constituent of the solution. To the mercuric-sodium nitrite solution, filtered from the mercurous chloride, dilute ammonia is gradually added until in slight excess. A cream-coloured, flocculent, but somewhat dense precipitate is produced, which is washed on a filter by aid of the suction-pump. Being slightly decomposed in the steam-oven, it has to be dried over sulphuric acid, and as it then collects into compact lumps, these are broken up and again exposed in the desiccator in order to facilitate the drying. The dry salt is pale yellow.

Nitrogen was determined by combustion with oxide of copper and chromate of lead. Although the analyses of the salt are not sufficient to decide the point, there is strong presumption in favour of the salt being anhydrous, as there is no guarantee that all moisture was removed from the preparations analysed :

	Mercury.	Nitrogen.
$2\text{NHg}_2\text{NO}_2, \text{H}_2\text{O}$ requires .....	83.68	5.85
	84.13	5.99
	84.64	6.02
	84.87	5.92
Found .....	85.30	6.00
	85.94	—
	86.02	—
$\text{NHg}_2\text{NO}_2$ requires .....	86.96	6.08

When heated in a bulb-tube, the salt decomposes without fusing,

x x 2

giving off nitrous fumes, mercury, and water, and leaving a yellowish residue, mostly mercuric oxide.

Hofmann and Marburg find that 'infusible white precipitate' yields the whole of its nitrogen as ammonia when it is heated at  $130^{\circ}$  for half-an-hour or more with a 20 per cent. solution of potassium hydroxide. I have repeated their experiments and can confirm their experience, having obtained 5.36 per cent., calculation giving 5.57. Dimercurammonium nitrite, however, could not be made to yield more than 2.5 per cent. of nitrogen by this treatment, whilst theory requires 3 per cent.

*New Mercuric Ammonium Chloride and Bromide.*—Like other salts of its kind, dimercurammonium nitrite dissolves readily in warm hydrochloric acid or hydrobromic acid; nitrous fumes escape, and the solution leaves, when evaporated, a white, crystalline mass which volatilises slowly, even on the water-bath. It proves to be a new mercury and ammonium salt, chloride, or bromide, according to the acid used, having the composition shown by the formula  $2\text{HgCl}_2, \text{NH}_4\text{Cl}$  or  $2\text{HgBr}_2, \text{NH}_4\text{Br}$ . The double chloride fuses and sublimes at a gentle heat, and is very soluble in water. The double bromide is decomposed by water into its constituent salts, and when the sparingly soluble mercuric bromide has been dissolved again by stirring it with the boiling solution of ammonium bromide, it separates as the solution cools in white, nacreous crystals. The presence of free acid seems to be necessary for the formation of these double salts, and I have, in fact, been able to prepare the double bromide by dissolving the single salts in the indicated proportions in presence of hydrobromic acid and evaporating the solution, but I have not succeeded in a similar way in getting the double chloride. The double bromide forms prisms and tablets, probably triclinic. The results of analyses of the two double salts are as follows:

	Mercury.	Chlorine.	Nitrogen.
Calc. for $2\text{HgCl}_2, \text{NH}_4\text{Cl}$ .....	67.17	29.81	2.35
Found .....	67.92	29.00	1.96
„ .....	67.94	29.20	—
„ .....	67.20	29.42	—
	Mercury.	Bromine.	Nitrogen.
Calc. for $2\text{HgBr}_2, \text{NH}_4\text{Br}$ .....	48.90	48.90	1.71
Found .....	49.29	48.31	1.66
„ ..	49.38	47.86	—
„ .....	48.65	—	—

*Production of Dimercurammonium Chloride and Bromide from the above-described Double Salts.*—When the double chloride is stirred with excess of dilute solution of potassium hydroxide, it gives a pale yellow precipitate having the composition of, and being apparently

identical with, André's half-hydrated dimercurammonium chloride,  $2\text{NHg}_2\text{Cl}\cdot\text{H}_2\text{O}$ , according to the results of analysis, which were :

	Mercury.	Chlorine.	Nitrogen.
Calc. ....	87.25	7.74	3.05
Found .....	87.10	7.54	2.90
„ .....	87.94	—	—
„ .....	87.06	—	—

It may be heated to  $150^\circ$  without appreciably losing water. The filtrate from this precipitate contains exactly four-fifths of the chlorine of the double salt; found: 24.10 and 23.98, instead of  $23.85 = 4/5$  of 29.81 per cent.

When treated with excess of potassium hydroxide, the double bromide yields a deep red precipitate which has the composition expressed by  $2\text{NHg}_2\text{Br}\cdot\text{H}_2\text{O}$ , after drying at  $100^\circ$ . There is left in the filtrate 39 per cent. of the bromine of the double salt, which is  $4/5$  of the total, 48.9. Analysis of the precipitate gave :

	Mercury.	Bromine.	Nitrogen.
Calc. ....	79.52	15.91	2.78
Found .....	79.82	15.66	2.60
„ .....	79.97	16.10	2.54

*New Mercuric-ammonium Chlorobromide.*—When dimercurammonium bromide is dissolved in hydrochloric acid and the solution concentrated, the double salt,  $2\text{HgCl}_2\cdot\text{NH}_4\text{Br}$ , is obtained. Dimercurammonium bromide is re-obtained quantitatively by mixing this salt in solution with excess of dilute potassium hydroxide, all the chlorine, and no bromine, remaining in solution. Thus, 22.37 and 23.02 per cent. of chlorine were found in solution instead of 22.19, given in the subjoined table :

	Mercury.	Chlorine.	Bromine.	Nitrogen.
Calc. ....	62.50	22.19	12.50	2.19
Found .....	63.01	20.89	12.71	1.97
„ .....	63.5	—	—	—
„ .....	62.89	—	—	—

It is somewhat remarkable that the compound dimercurammonium chloride, when dissolved in hydrobromic acid and the solution concentrated, does not yield the bromochloride,  $2\text{HgBr}_2\cdot\text{NH}_4\text{Cl}$ , but the double bromide,  $2\text{HgBr}_2\cdot\text{NH}_4\text{Br}$ ; in other words, the chlorine is replaced by bromine. This reaction has its analogy in Field's experiment (Trans., 1858, 11, 234).

*Dimercurammonium-mercuric Bromide and Chloride.*—By adding potassium hydroxide, gradually and not in excess, to a boiling solution of the double bromide of mercury and ammonium, I have obtained the

salt  $2\text{NHg}_2\text{Br}, \text{HgBr}_2$ , which is, however, not always easy to get. The analyses of three distinct preparations are given below:

	Mercury.	Bromine.	Nitrogen.
Calc. ....	74.19	23.74	2.07
Found ....	73.55	24.30	2.35
„ ....	72.65	22.82	—
„ ....	73.44	21.99	—

I have not succeeded in getting the corresponding chloride in a pure state, but a yellowish-white precipitate, which can hardly be anything else but impure dimercurammonium-mercuric chloride, is obtained when, to a dilute solution of the mercuric-ammonium chloride, above described, potassium hydroxide is very gradually added with care, to avoid using it in excess. The calculated percentage composition of  $2\text{NHg}_2\text{Cl}, \text{HgCl}_2$  is mercury, 85.5; chlorine, 12.1; and nitrogen, 2.4, whilst the mean numbers of some half-dozen fairly concordant analyses of as many different preparations of this precipitate are, respectively, 84.5, 11.3, and 3.0. The same numbers would express the percentage composition of the following mixture, which, it will be seen, consists mainly of dimercurammonium-mercuric chloride,  $2\text{NHg}_2\text{Cl}, \frac{2}{3}\text{HgCl}_2 + \frac{1}{3}\text{NH}_4\text{Cl} + \frac{2}{3}\text{H}_2\text{O}$ .

In conclusion, I wish to express most cordial thanks to Professor Edward Divers, F.R.S., for some valuable suggestions, which have greatly aided me in putting this paper together.

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## LXVII.—*Influence of Substitution on the Reactivity of the Aromatic m-Diamines.*

By GILBERT THOMAS MORGAN, D.Sc.

It has already been shown in a recent communication (this vol., p. 86) that the reactivity of the aromatic *m*-diamines towards diazonium salts may be very considerably modified by the introduction of substituent radicles into certain positions in the aromatic nucleus. It was found that the symmetrically disubstituted *m*-diamines furnished only small quantities of azo-compounds, whereas their isomerides containing a free para-position with respect to an amino-group gave rise to azo-derivatives in theoretical quantities.

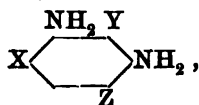
The behaviour of the homologues of *m*-phenylenediamine on methylation has now been investigated, and the results indicate that the diminution in reactivity, brought about by the introduction of radicles into the para-ortho-positions with respect to the nitrogen atoms, is equally noticeable when the diamines are subjected to the action of alkylating agents.

The influence of substitution on the methylation of primary aromatic amines has already been studied by Pinnow (*Ber.*, 1897, 30, 3110; 1899, 32, 1401; 1901, 34, 1129), who treated the hydrochlorides or hydrobromides of these bases with methyl alcohol at 145—190°. Under these conditions, a monoamine in which the two ortho-positions adjacent to the nitrogen atom are both unoccupied yields a mixture of tertiary base and quaternary salt. If, however, the amine contains a substituent radicle in one of these positions, it gives rise to a dialkyl derivative only. It remained uncertain as to whether this rule holds for the diamines, for although the methylation of benzidine and the three phenylenediamines had been investigated (Pinnow, *loc. cit.*), the research was not extended to the homologues of these diamines.

An examination of *m*-tolylenediamine (2:4-diaminotoluene) and 4:6-diamino-*m*-xylene from this standpoint shows that Pinnow's generalisation may be extended to the *m*-diamines, the former of these bases furnishing a mixture of 2:4-tetramethyldiaminotoluene and the quaternary hydrochloride or hydrobromide, the latter yielding 4:6-tetramethyldiamino-*m*-xylene as the sole product.

A comparative experiment made with *m*-phenylenediamine led to the production of the tertiary base and the quaternary salt together with fluorescent, tarry impurities, the alkylation taking place more energetically, but less smoothly, than with the homologous diamines. Diaminomesitylene, when treated in this manner, remains practically unchanged.

These results indicate that the successive introduction of methyl groups into the three positions (X, Y, Z) adjacent to the two nitrogen atoms of *m*-phenylenediamine,

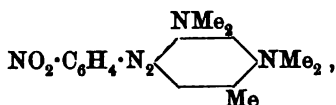


is attended by a well-marked diminution in the reactivity of the diamine towards methyl chloride or bromide, the interaction being prevented when the substitution of the three contiguous hydrogen atoms is complete (compare E. Fischer and Windaus, *Ber.*, 1900, 33, 345 and 1967).

The tertiary diamines obtained in this investigation exhibit a gradation in properties similar to that observed in the case of the

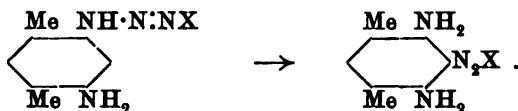
corresponding primary bases; their reactivity diminishes as the homologous series is ascended. When distilled under diminished pressure, these tertiary bases are obtained as almost colourless, oily liquids; tetramethyl-*m*-phenylenediamine, however, rapidly darkens on exposure to light and air, whilst tetramethyl-4:6-diamino-*m*-xylene remains unchanged even after a year. The intermediate homologue, tetramethyl-2:4-diaminotoluene, becomes darker on keeping, but much less rapidly than the first member of the series.

The two lower homologues readily react with diazo-compounds, and the azo-colours obtained by the action of diazotised primulin closely resemble those produced from the corresponding primary diamines. 2:4-Tetramethyldiaminotoluene readily condenses with *p*-nitrobenzene-diazonium chloride, giving rise to *p*-nitrobenzene-5-azo-2:4-tetramethyldiaminotoluene,

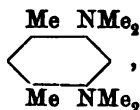


in theoretical yield, and similar results are obtained with other diazonium salts. 4:6-Tetramethyldiamino-*m*-xylene does not combine with diazotised primulin, and when treated with a solution of *p*-nitrobenzenediazonium chloride containing sodium acetate, it remains entirely unchanged.

This inactivity of the symmetrically disubstituted tertiary diamine should be contrasted with the behaviour of 4:6-diamino-*m*-xylene under similar conditions (this vol., p. 88), for it furnishes additional evidence in support of the view that the readily decomposable initial product of the action of a diazonium salt on the primary base is an unstable diazoamine which subsequently undergoes transformation into tarry products and a small amount of azo-compound,



In the present instance, however, where the initial attachment of the diazo-residue to one of the nitrogen atoms is rendered impossible by the complete alkylation of the amino-radicles,

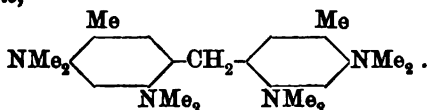


the production of an *o*-azo-derivative is altogether prevented.

This hindrance to the formation of azo-derivatives, due to alkylation,

although so strikingly manifested in the case of the preceding tertiary diamine, does not obtain among the tertiary amines containing a free para-position with respect to nitrogen. As already indicated, 2:4-tetramethyldiaminotoluene yields azo-compounds quite as readily as 2:4-tolylenediamine itself, in this respect resembling dimethylaniline, which is employed in the production of several well-known azo-colouring matters.

The difference in reactivity between 2:4-tetramethyldiaminotoluene and 4:6-tetramethyldiamino-*m*-xylene is also demonstrated by their behaviour towards formaldehyde. The lower homologue readily interacts with this reagent, yielding 2:4:2':4'-octamethyltetraminoditolyl-5:5'-methane,



The disubstituted tertiary diamine, on the contrary, is not affected by formaldehyde, even when the experiment is carried out under pressure at high temperatures in the presence of excess of acetic anhydride.

## EXPERIMENTAL.

### *Methylation of m-Tolylenediamine.*

*m*-Tolylenediamine hydrobromide and an excess of alcohol (6—7 mols.) were heated in sealed tubes at 180° until the product on cooling no longer deposited a crystalline hydrobromide, this result being usually obtained in 8 to 10 hours. The pressure was released after 4 hours' heating in order to prevent the tubes from bursting. The product, after being heated on the water-bath to remove the unaltered methyl alcohol, was treated with excess of potassium hydroxide solution, the oil which separated being extracted with ether. The liquid of high boiling point remaining after the removal of the ether distilled at 254—259° under 757 mm. pressure, the greater portion boiling between 255° and 256°.

2:4-Tetramethyldiaminotoluene, thus obtained as a pale brownish-yellow oil, was further purified by repeated distillation under reduced pressure and finally boiled at 148—150° under 24—26 mm. pressure; it has a sp. gr. 0.9661 at 24° and does not solidify at -10°.

The *platinichloride*,  $C_{11}H_{18}N_2 \cdot H_2PtCl_6$ , separates from aqueous solutions in stellar aggregates of slender, transparent, yellow prisms; it rapidly darkens when left in contact with the mother liquor, and is decomposed by boiling water, evolving formaldehyde and yielding a dark red solution. The salt when dried at 80—90° gave the following numbers on analysis:



0.2542 gave 0.0840 Pt.  $Pt = 33.04$ .

$C_{11}H_{20}N_2Cl_6Pt$  requires  $Pt = 33.16$  per cent.

The *picrate* crystallises from ethyl acetate in hard, transparent, yellow prisms, and melts at  $162-163^\circ$ ; it is formed by the union of picric acid and the diamine in molecular proportion:

0.1479 gave 22.4 c.c. moist nitrogen at  $16^\circ$  and 760 mm.  $N = 17.66$ .

$C_{17}H_{21}O_7N_5$  requires  $N = 17.20$  per cent.

The *methobromide*,  $NMe_2 \cdot C_6H_3Me \cdot NMe_3Br$ .—The solution of potassium hydroxide employed in liberating the tertiary base assumed a dark brown colour, and when saturated with the solid reagent yielded a heavy brown oil which rapidly solidified to a mass of brown, acicular crystals. This substance, which contained bromine, was identified as the quaternary bromide by conversion into the corresponding chloride and subsequent formation of the platinichloride. A solution of the bromide was triturated with moist silver oxide and filtered, the filtrate being then treated with hydrochloric acid and platinic chloride.

The *platinichloride*,  $NMe_2 \cdot C_6H_3Me \cdot NMe_3 \cdot HPtCl_6$ , which separates out may be crystallised from hot water without decomposition; it is deposited on cooling in transparent, brownish-yellow prisms and is far more stable than the corresponding salt of the tertiary base:

0.2269 gave 0.0736 Pt.  $Pt = 32.43$ .

0.1861 „ 0.0603 Pt.  $Pt = 32.40$ .

$C_{12}H_{22}N_2Cl_6Pt$  requires  $Pt = 32.39$  per cent.

The remainder of the methobromide was converted into the tertiary diamine either by heating with ammonia under pressure (Pinnow, *loc. cit.*), or by treating the quaternary salt with moist silver oxide and evaporating down the filtered solution of the quaternary ammonium hydroxide.

The methylation follows the same course when *m*-tolylenediamine hydrochloride is employed, the product in this case being a mixture of the tertiary base with the methochloride.

#### *Methylation of 4:6-Diamino-m-xylene.*

A mixture of 4:6-diamino-*m*-xylene hydrochloride and excess of methyl alcohol was heated in sealed tubes at  $180^\circ$  until it remained viscid on cooling; the product, after being heated on the water-bath to remove excess of methyl alcohol, was rendered alkaline with strong potassium hydroxide solution and extracted with ether. The ethereal extract, when dried over potassium hydroxide, and subsequently distilled, yields an oily base boiling at  $243-245^\circ$  under 757 mm. pressure.

4:6-Tetramethyldiamino-*m*-xylene, a pale brownish-yellow oil boiling

at 124—125° under 12 mm. pressure, remains liquid at -10° and has a sp. gr. 0.9434 at 18°; it does not darken perceptibly when kept for 12 months in diffused light.

The *platinichloride*,  $C_6H_2Me_2(NMe_2)_2 \cdot H_2PtCl_6$ , separates from an aqueous solution of its generators in transparent, orange-yellow, acicular prisms; it is moderately soluble in water, melts indefinitely above 200°, and is far more stable than the corresponding salt of 2:4-tetramethyldiaminotoluene; it may be crystallised from hot water without decomposition, and separates in reddish-orange needles often more than an inch in length:

0.2682 gave 0.0861 Pt.  $Pt = 32.10$ .

$C_{12}H_{22}N_2Cl_6Pt$  requires  $Pt = 32.39$  per cent.

The *picrate*,  $C_6H_2Me_2(NMe_2)_2 \cdot C_6H_2(NO_2)_3 \cdot OH$ , obtained by mixing together alcoholic solutions of its generators, crystallises from ethyl acetate in hard, transparent, yellow, rhombic prisms, sparingly soluble in the alcohols, but dissolving more readily in acetone; when rapidly heated, it melts at 202—203°, but slowly decomposes when maintained at 193—195°:

0.22 gave 30.5 c.c. moist nitrogen at 14° and 756 mm.  $N = 16.22$ .

$C_{18}H_{28}O_7N_5$  requires  $N = 16.62$  per cent.

4:6-Tetramethyldiamino-1:3-xylene is produced with equal readiness from 4:6-diamino-*m*-xylene hydrobromide and methyl alcohol, the tertiary base being the sole product whether the hydrochloride or the hydrobromide is employed.

Diaminomesitylene hydrochloride, when heated with methyl alcohol, does not undergo methylation, the greater part of the primary diamine being recovered on working up the product.

In preparing this diamine from dinitromesitylene (m. p. 86°) by the action of iron filings and water acidified with hydrochloric acid, it was found that only one of the nitro-groups became involved in the reduction, so that nitromesidine crystallised out from the filtered solution in golden-yellow needles melting at 70°. The complete reduction was accomplished by means of excess of tin and hot hydrochloric acid, but even with this reagent the action was very slow.

Comparative experiments made on the methylation of *m*-phenylenediamine showed that the action is less under control than in the case of the homologous diamines, the production of the tertiary base and quaternary salt being attended by the formation of fluorescent, tarry impurities.

The tertiary base, tetramethyl-*m*-phenylenediamine, after treatment with acetic anhydride to remove any secondary amines, was purified by repeated rectification under reduced pressure, and finally ob-

tained as a brownish-yellow oil rapidly darkening on exposure, boiling at 151—157° under 26 mm. pressure, and having a sp. gr. 0.9934 at 27° (compare Romburgh, *Rev. Trav. Chim.*, 1888, 7, 3; Wurster and Morley, *Ber.*, 1879, 12, 1814).

*Tertiary m-Diamines and Diazonium Salts.*

When a piece of cotton cloth impregnated with diazotised primulin is introduced into an aqueous solution of tetramethyl-*m*-phenylenediamine or its tolylene homologue, a brownish-red azo-colouring matter is developed on the fibre, the colour of which closely resembles that obtained by the use of the corresponding unalkylated *m*-diamine. 4:6-Tetramethyldiamino-*m*-xylene, on the other hand, does not combine with this diazo-compound.

*p*-Nitrobenzene-5-azo-2:4-tetramethyldiaminotoluene.—A solution of *p*-nitrobenzenediazonium chloride, when added to 2:4-tetramethyldiaminotoluene dissolved in cold dilute hydrochloric acid, produced a dark-red precipitate the formation of which was completed by the addition of excess of sodium acetate. This insoluble product was crystallised from alcohol, separating from its solutions in dark-green leaflets with a bronze lustre; the yield was quantitative.

*p*-Nitrobenzene-5-azo-2:4-tetramethyldiaminotoluene is sparingly soluble in cold alcohol, dissolving more readily in ethyl acetate and crystallising from this solvent in leaflets melting at 126—127°. Its solutions in the organic solvents have a deep purple colour and the azo-compound dissolves in cold concentrated sulphuric acid to an intense brownish-red solution:

0.1808 gave 33.4 c.c. moist nitrogen at 15° and 756 mm.  $N = 21.52$ .

$C_{17}H_{21}O_2N_5$  requires  $N = 21.41$  per cent.

The hydrochloride and platinichloride are red precipitates, the nitrate crystallises from alcohol in deep red leaflets, the picrate separates from the same solvent in red needles.

When the preceding experiment was repeated with 4:6-tetramethyldiamino-*m*-xylene, the introduction of the *p*-nitrobenzenediazonium chloride produced no effect on the solution of the tertiary diamine. After remaining for 24 hours, the mixture deposited a tarry product, due to the gradual decomposition of the diazonium base set free by the sodium acetate, but the filtered solution still contained the unaltered diamine. This base was completely recovered by treating the solution with excess of potassium hydroxide and extracting with ether, being precipitated in the form of its picrate by the addition of an alcoholic solution of picric acid to the ethereal extract. The yield of

recrystallised picrate obtained in this operation was 90 per cent. of the theoretical.

*Tertiary m-Diamines and Formaldehyde.*

Six grams of 2 : 4-tetramethyldiaminotoluene dissolved in 20 grams of acetic anhydride were treated with 2 c.c. of 40 per cent. formaldehyde solution and allowed to remain for 20 hours ; the mixture was then heated to boiling, subsequently cooled, and rendered alkaline with excess of ammonia. The oily product which first separated rapidly solidified, and, after drying on a porous tile, was crystallised from ethyl acetate or alcohol.

2 : 4 : 2' : 4'-Octamethyltetraminoditolyl-5 : 5'-methane separates in well-defined, transparent, colourless prisms, either obliquely truncated or terminated by pyramids ; the crystals often exhibit external twinning and melt at 86° :

0.1473 gave 0.4037  $\text{CO}_2$  and 0.1322  $\text{H}_2\text{O}$ : C = 74.74 ; H = 9.97.

0.1833 ,, 24.6 c.c. moist nitrogen at 18° and 764 mm. N = 15.58.

$\text{C}_{23}\text{H}_{28}\text{N}_4$  requires C = 75.00 ; H = 9.78 ; N = 15.21 per cent.

The tetramine is readily soluble in most organic solvents with the exception of light petroleum ; it dissolves in dilute aqueous solutions of the mineral acids, and yields a colouring matter of the acridine series when heated with hydrochloric acid at 150°. It is not an analogue of the leuco-base of malachite-green, for it does not give rise to a colouring matter of this type when oxidised with lead peroxide and acetic acid.

The *picrate* separates from ethyl acetate in spherical aggregates of hard, transparent, yellow crystals and melts at 147—148°.

4 : 6-Tetramethyldiamino-*m*-xylene, when dissolved in acetic anhydride and treated with formaldehyde solution, remains unaltered even when an excess of the reagents is employed in sealed tubes at 150—170° ; the unchanged base recovered from the mixture boils at 243—248° (corr. 245°), and yields the characteristic picrate (m. p. 202—203°).

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LXVIII.—*The Influence of Certain Acidic Oxides on the Specific Rotations of Lactic Acid and Potassium Lactate.*

By GEORGE GERALD HENDERSON and DAVID PRENTICE, Ph.D.

IN the course of an investigation of the compounds produced by the action of certain acidic oxides on metallic salts of hydroxy-acids in aqueous solution, which has formed the subject of previous communications to the Society (Trans., 1895, 67, 102 and 1030; 1896, 69, 1451; 1899, 75, 542), we endeavoured to prepare arsenio- and antimonio-lactates by dissolving arsenious and antimonious oxides respectively in hot aqueous solutions of various metallic lactates, but did not succeed in isolating any definite compounds, although it was found that the solutions were capable of dissolving considerable quantities of the former oxide. Similar experiments with other acidic oxides were equally unsuccessful, except in one instance, where a crystalline potassium molybdilactate,  $\text{MoO}_2(\text{C}_3\text{H}_4\text{O}_3\text{K})_2$ , was obtained. It was unfortunate that no other derivatives of lactic acid could be prepared in a sufficiently pure form to justify us in assigning formulæ to them, because, as that was the only hydroxy-acid used in our experiments which contained one alcoholic hydroxyl and one carboxyl group, the determination of the composition of its derivatives was of importance with regard to the bearing of the results on our general conclusions concerning the constitution of the "tartar emetic" class of derivatives of the other hydroxy-acids (malic, tartaric, citric, and mucic) which came within the scope of the research. However, another method of investigation is available in the case of optically active acids, by means of which it is possible to draw conclusions regarding the composition of derivatives formed in solution, even although these cannot be obtained in a form suitable for analysis.

It is well known that the dissolution of such optically inactive compounds as boric acid or antimonious oxide in solutions of the optically active modifications of malic and tartaric acids, or of their salts, produces more or less marked alterations in the specific rotations of the solutions. There can be no doubt that these alterations are due to the formation of new optically active compounds by interaction of the inactive oxides and the active acids, because in many instances the substances of which the existence is indicated by the rotations of their solutions can be obtained in the solid state. This is true, for example, of many boro-, arsenio-, and antimonio-tartrates. Moreover, Rosenheim and Itzig (*Ber.*, 1900, 33, 707) have recently confirmed in this way the existence in aqueous solution of the alkali molybditartrates of the

type  $\text{MoO}_3(\text{C}_4\text{H}_4\text{O}_6\text{M}')_2$ , which were prepared by one of us some time ago, and Itzig (*Ber.*, 1901, 34, 1391) has found that the maximum rotation of a solution of molybdenum trioxide in aqueous ammonium hydrogen malate is obtained when the substances are present in the proportions necessary for the formation of the salt  $\text{MoO}_3(\text{C}_4\text{H}_4\text{O}_6\cdot\text{NH}_4)_2$ , which was formerly isolated and described by one of us. Therefore, with the hope of gaining the desired information by this method, we have begun to examine the influence of various acidic oxides on the rotations of solutions of optically active lactic acid and its potassium salt. The present paper contains the results of the experiments with arsenious, antimonious, and boric oxides.

Any compound formed by the interaction of one of these oxides and a metallic lactate would probably be of the type  $\text{CH}_3\cdot\text{CHO}(\text{RO})\cdot\text{CO}_2\text{M}'$  (*Trans.* 1899, 75, *loc. cit.*). No such compound is yielded by antimonious oxide, which was found to be almost insoluble in hot solutions of potassium lactate. Arsenious oxide, on the contrary, is very readily dissolved by hot aqueous potassium lactate, and as the quantity of oxide in the solution is increased, the rotation becomes greater and reaches a maximum when the solution contains 1 mol.  $\text{As}_2\text{O}_3$  to 4 mols.  $\text{C}_3\text{H}_5\text{O}_5\text{K}$ , that is, when the substances are present in the proportion requisite for the formation of an arseniolactate of potassium of the formula  $\text{CH}_3\cdot\text{CHO}(\text{AsO})\cdot\text{CO}_2\text{K}$ . It is true that the change produced in the rotation of the solution of potassium lactate by dissolving arsenious oxide in it is not great, but then, on the other hand, the oxide is dissolved in much greater quantity than by water, and on the whole the conclusion seems justified that the solution contains a new compound. When boric acid is dissolved in a solution of potassium lactate, a marked change in the rotation is produced. If increasing quantities are added to a solution of the dextrorotatory salt, the rotation diminishes, until finally, when the boric acid and the salt are present in the quantities required for the formation of a borolactate of potassium of the formula  $\text{CH}_3\cdot\text{CHO}(\text{Bo})\cdot\text{CO}_2\text{K}$ , the solution is almost equally strongly levorotatory. At first sight, the change in the rotation would appear to be due simply to the liberation of lactic acid, but then the rotation of the solution is much greater than one of lactic acid of equivalent strength, and, moreover, boric acid has also a marked effect on the rotation of a solution of lactic acid. It is probable therefore that borolactic acid or its potassium salt is formed when boric acid is dissolved in a solution of lactic acid or potassium lactate.

For the preparation of *d*- and *l*-lactic acids, we adopted Purdie's process for the resolution of the inactive acid, namely, crystallisation of the double zinc ammonium salts (*Purdie, Trans.*, 1893, 63, 1142; *Purdie and Walker, Trans.*, 1895, 67, 616). The process, although necessarily somewhat tedious, gave excellent results in the hands of

several workers when the requisite precautions were strictly observed, and our work was much lightened by Professor Purdie's kindness in providing us with specimens of the pure active zinc ammonium salts for starting the crystallisations, and in giving many useful hints on details of procedure. In addition to the method prescribed by Purdie for preparing the active acids from their pure zinc salts (conversion of the zinc into the calcium salt, decomposition of the latter with the calculated quantity of sulphuric acid, and extraction of the lactic acid with ether), we employed the following process. A solution of the pure zinc salt was saturated with hydrogen sulphide, the precipitated zinc sulphide removed by filtration, and the filtrate concentrated at the ordinary temperature in a vacuum desiccator containing sticks of caustic soda until all the sulphuretted hydrogen had disappeared, which required about forty-eight hours. The solution was finally evaporated to a small bulk on the water-bath and filtered. Judging by its rotation, the acid thus prepared was quite as pure as that obtained by the other process.

The solutions of which the rotations were to be examined were all prepared in practically the same way. For convenience, the solutions of lactic acid and potassium lactate were made up of normal and semi-normal strength. The required quantity of the solution of the lactate was measured into a small flask, the calculated weight of the oxide added, and the liquid kept boiling gently for about an hour. The solution and the washings of the flask were then transferred to a graduated flask, if necessary through a small filter, and the liquid made up to the mark. All the polarimetric observations were made at the same temperature, 20°. The length of the tube of the polarimeter was 200 mm.

#### *Experiments with Antimonious Oxide.*

The experiments with antimonious oxide showed that no antimonio-lactate is formed, at least under the conditions observed. Antimonious oxide was found to be almost insoluble in solutions of potassium lactate, even after prolonged boiling; thus, for example, 25 c.c. of a normal solution of the salt dissolved only 2.5 mg. of oxide, and the same quantity of a semi-normal solution only 3 mg. The rotations of the solutions were practically unaffected by the presence of a trace of the oxide.

#### *Experiments with Arsenious Oxide.*

In the first set of experiments we used a semi-normal solution of potassium lactate ( $c = 6.405$ ), from which solutions containing arsenious oxide in the proportions of  $\frac{1}{4}$  mol.,  $\frac{1}{2}$  mol.,  $\frac{3}{4}$  mol., and 1 mol.  $As_2O_3$

respectively to 1 mol.  $C_3H_5O_3K$  were prepared in the way already described. The solution was found to be saturated with arsenious oxide when the latter was present in the proportion of 1 mol. of oxide to 4 mols. of lactate, for although a still larger quantity was soluble in the hot liquid, the excess separated in the crystalline state as the liquid cooled.\* The saturated solution contains the substances in the proportion necessary for the formation of potassium arsenio-lactate,  $(AsO)C_3H_4O_3K$ , and the maximum rotation was found at this point. However, as will be seen from the following figures,† no very marked change was produced in the rotation of the lactate, which is given for comparison :

Weight of $C_3H_5O_3K$ in 25 c.c. of solution.	Weight of $As_2O_3$ added.	Molecular proportions of $C_3H_5O_3K$ and $As_2O_3$ .	$\alpha_D^{20^\circ}$ .	$[\alpha]_D^{20^\circ}$ .
1.6013	—	—	+1.35°	+10.54°
"	0.3094	4 : $\frac{1}{2}$	1.405	9.19
"	0.6188	4 : $\frac{1}{3}$	1.42	7.99
"	0.9282	4 : $\frac{2}{3}$	1.44	7.11
"	1.2375	4 : 1	1.47	6.47

Two other sets of observations were made with solutions of different strength. In the first, in which a normal solution of potassium lactate ( $c=12.81$ ) was used, readings of the rotation were only taken up to the point at which  $\frac{1}{2}$  mol.  $As_2O_3$  was present for each 4 mols.  $C_3H_5O_3K$ , because although the solution was capable of dissolving larger quantities when hot, part of the oxide always crystallised out on cooling. At this point, the rotation of the solution had increased from +2.58° to +2.77°. In the last series of observations, the strength of the lactate solution was one-fourth normal ( $c=3.2025$ ). In this case, it was found that, although larger quantities were dissolved on heating, the maximum quantity of arsenious oxide which was permanently retained in solution corresponded with that necessary for the formation of the compound  $(AsO)C_3H_4O_3K$ . At this point, the rotation had increased from +0.65° to +0.72° ( $[\alpha]_D^{20^\circ} + 6.33^\circ$ ).

For purposes of comparison, observations were also made of the rotations of solutions of arsenious oxide in semi-normal lactic acid ( $c=4.5$ ). As will be seen from the following figures, the effect of the

\* In some cases, the excess of arsenious oxide did not separate until the liquid had been kept for several days at the ordinary temperature.

† Some of the experiments were made with *d*-, others with *l*-lactic acid, or their salts, but for simplicity the results have been stated as if *l*-lactic acid, or potassium *l*-lactate, had been used in each case.



# 662 ROTATIONS OF LACTIC ACID AND POTASSIUM LACTATE.

presence of the arsenious oxide was slightly to diminish the rotation of the solution :

Weight of $C_3H_5O_2$ in 25 c.c. of solution.	Weight of $As_2O_3$ added.	Molecular proportions of $C_3H_5O_2$ and $As_2O_3$ .	$\alpha_D^{20}$ .	$[\alpha]_D^{20}$ .
1.125	—	—	-0.187°	-2.01°
„	0.6188	4 : $\frac{1}{2}$	0.08	0.57
„	1.2375	4 : 1	0.07	0.37

## Experiments with Boric Acid.

For the experiments with boric acid, a normal solution ( $c=12.81$ ) of potassium lactate was employed. The addition of boric acid, in the quantities given in the following table, produced marked changes in the rotation of the solution, which reached a maximum when the boric acid and lactate were present in the proportion (1 mol. : 1 mol.) necessary for the formation of potassium borolactate  $(BO)C_3H_5O_2K$ . At this point, at which the solution was saturated with boric acid, the solution, which was originally dextrorotatory, had become lævoro-rotatory :

Weight of $C_3H_5O_2K$ in 25 c.c. of solution.	Weight of $B(OH)_3$ added.	Molecular proportions of $C_3H_5O_2K$ and $B(OH)_3$ .	$\alpha_D^{20}$ .	$[\alpha]_D^{20}$ .
3.2025	—	—	+2.58°	+10.05°
„	0.3875	1 : $\frac{1}{2}$	+1.54	+5.36
„	0.7750	1 : $\frac{1}{2}$	+0.473	+1.48
„	1.1625	1 : $\frac{1}{2}$	-0.27	-0.77
„	1.5500	1 : 1	-1.076	-2.83

It might appear that these changes were due to the liberation of lactic acid. In order to determine this, the observations on p. 663 were made on the effect of boric acid on the rotation of a normal solution of lactic acid ( $c=9.0$ ).

At this point, the solution was saturated with boric acid. Another reading was therefore taken with a semi-normal solution of lactic acid, which contained, in 25 c.c., 1.125 grams  $C_3H_5O_2$  and 0.7750 gram  $B(OH)_3$  (1 mol. : 2 mols.). The specific rotation was found to be  $-2.87^\circ$ .

The examination of the effect of molybdic, tungstic, and other acidic oxides on the rotations of lactic acid and potassium lactate is at present in progress.

Weight of $C_8H_6O_3$ in 25 c.c. of solution.	Weight of $B(OH)_3$ added.	Molecular proportions of $C_8H_6O_3$ and $B(OH)_3$ .	$\alpha_D^{20}$ .	$[\alpha]_D^{20}$ .
2.25	—	—	-0.34°	-1.88°
"	0.8875	1 : $\frac{1}{4}$	0.73	3.46
"	0.7750	1 : $\frac{1}{2}$	0.92	3.80
"	1.1625	1 : $\frac{3}{4}$	1.07	3.92

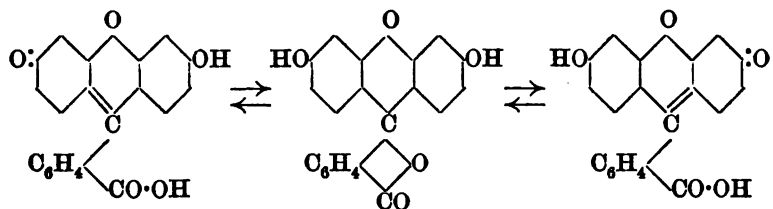
We take this opportunity of expressing our thanks to Mr. James Prentice for much assistance given in the course of this work.

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## LXIX.—Oxonium Salts of Fluoran and its Derivatives.

By J. T. HEWITT AND J. N. TERVET.

Two years ago (Proc., 1900, 16, 3, and *Zeit. physikal. Chem.*, 1900, 34, 1), one of the authors of the present communication proposed a theory connecting the fluorescence of certain organic compounds with their constitution. Briefly stated, this was as follows. If a substance can be converted into a tautomeric modification of greater free energy by two equal displacements in opposite directions, the molecules will vibrate between the two extreme positions, and radiant energy of a particular wave-length taken up by the molecules will be emitted with a different wave-length. It was shown that generally the fluorescent dye-stuffs conformed to this type of constitution; the molecules of fluorescein in solution may be compared with a pendulum swinging between two extreme positions:

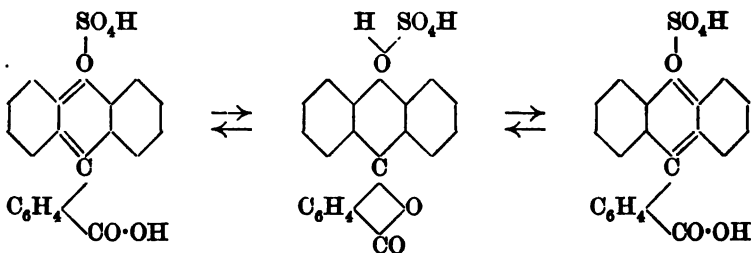


The parent substance of fluorescein, namely, fluoran (R. Meyer, *Ber.*, 1891, 24, 1412; 1892, 25, 1385), or phenolphthalein anhydride

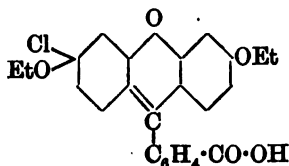
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(Baeyer, *Annalen*, 1882, 212, 349), is colourless, and gives colourless non-fluorescent solutions in neutral solvents.

If, however, it be dissolved in concentrated sulphuric acid, a yellow solution exhibiting a brilliant green fluorescence is produced, and to explain this phenomenon, the formation of salts containing quadrivalent oxygen was assumed :



A similar assumption made in the case of xanthhydrol and allied compounds has been abundantly confirmed (Werner, *Ber.*, 1901, 34, 3300; Hewitt, *Ber.*, 1901, 34, 3819). The existence of salts derived from fluoran has, however, been regarded with suspicion in R. Meyer's *Jahrbuch der Chemie* (1901, 10, 438). This is, perhaps, the more surprising, seeing that Nietzki and Schröter (*Ber.*, 1895, 28, 56) obtained a yellow additive product from the lactonic diethyl ether of fluorescein (that is, diethoxyfluoran), to which, however, they assigned the constitution :



To settle the question, attempts have been made to isolate salts of fluoran and its derivatives with strong mineral acids, and the results obtained are here communicated.

**Fluoran Nitrate**,  $C_{20}H_{12}O_8, HNO_3$ .—Fluoran was warmed with excess of a mixture of colourless nitric acid (sp. gr. 1.36) and acetic anhydride. The substance went into solution with a yellow colour; on cooling, small, pale yellow crystals were deposited. The excess of acid was decanted, and the crystals dried on porous earthenware over sulphuric acid.

For analysis, the substance was decomposed by water, the fluoran collected, and dried until the weight was constant. The loss in weight represents the nitric acid with which the fluoran had combined :

0.1292 lost 0.0226  $HNO_3$ .  $HNO_3 = 17.49$ .

$C_{20}H_{12}O_8, HNO_3$  requires  $HNO_3 = 17.36$  per cent.

*Fluoran Sulphate*,  $C_{20}H_{12}O_8, H_2SO_4$ .—Fluoran dissolved when ground up with a mixture of strong sulphuric and glacial acetic acids. Careful addition of water produced a yellow precipitate, which was dried on porous earthenware :

0.3677 gave 0.2060  $BaSO_4$ .  $SO_4 = 23.17$ .

$C_{20}H_{12}O_8, H_2SO_4$  requires  $SO_4 = 24.12$  per cent.\*

We were unable to isolate a hydrochloride of fluoran.

*Dimethylfluoran Nitrate*,  $C_{22}H_{16}O_8, HNO_3$ .—Dimethylfluoran has already been described by Drewsen (*Annalen*, 1882, 212, 340). We prepared the material for our experiments by his method from *p*-cresol, phthalic anhydride, and sulphuric acid. The nitrate was obtained by finely grinding the substance with a mixture of nitric acid and acetic anhydride, and drying on porous earthenware. From a hot solution in a mixture of acetic anhydride and nitric acid, the substance separates in small, well-formed, yellow prisms, terminated obliquely and frequently twinned :

0.2628, on washing, lost 0.0407  $HNO_3$ .  $HNO_3 = 15.45$ .

$C_{22}H_{16}O_8, HNO_3$  requires  $HNO_3 = 16.11$  per cent.

*Dimethylfluoran Sulphate*,  $C_{22}H_{16}O_8, H_2SO_4$ .—This salt was prepared analogously to the fluoran sulphate. It forms a yellow, crystalline powder consisting of minute, short prisms :

0.3463 gave 0.1679  $BaSO_4$ .  $SO_4 = 19.83$ .

$C_{22}H_{16}O_8, H_2SO_4$  requires  $SO_4 = 22.53$  per cent.

*Dimethylfluoran Disulphate*,  $C_{22}H_{16}O_8, 2H_2SO_4$ , was obtained when dimethylfluoran and acetic acid were ground to a paste, concentrated sulphuric acid added, and the salt allowed to separate without the addition of water :

0.3670 gave 0.3286  $BaSO_4$ .  $SO_4 = 36.89$ .

0.3850 „ 0.3257  $BaSO_4$ .  $SO_4 = 34.86$ .

$C_{22}H_{16}O_8, 2H_2SO_4$  requires  $SO_4 = 36.64$  per cent.

Attempts to prepare a hydrochloride failed, although dimethylfluoran assumes a yellow colour when treated with concentrated hydrochloric acid.

*Fluorescein Hydrochloride*,  $C_{20}H_{12}O_5, HCl$ .—Fluorescein was ground to a paste with cold acetic anhydride and then exposed to a current of dry hydrogen chloride until all excess of acetic anhydride was removed. An orange powder was obtained. For analysis, the substance was dissolved in hot sodium carbonate solution, the fluorescein precipitated

\* Considering the unstable nature of the compounds produced, it is not surprising that in certain cases the analyses have only given approximate results.

by dilute nitric acid, and, after removal of the fluorescein, the chlorine estimated gravimetrically in the filtrate :

0.0900 gave 0.0326 AgCl.  $\text{HCl} = 9.21$ .

$\text{C}_{20}\text{H}_{12}\text{O}_5$ , HCl requires  $\text{HCl} = 9.16$  per cent.

*Fluorescein Sulphate*,  $\text{C}_{20}\text{H}_{12}\text{O}_5, \text{H}_2\text{SO}_4$ .—Fluorescein heated with sulphuric acid at  $100^\circ$  furnishes a substance to which the formula  $\text{C}_{20}\text{H}_{12}\text{O}_5, \text{SO}_3$  has been assigned by Baeyer (*Annalen*, 1876, 183, 27). The fact that the substance so obtained is immediately decomposed by water into fluorescein and sulphuric acid would suggest that the substance was a sulphate. Fluorescein, we find, gives a disulphate,  $\text{C}_{20}\text{H}_{12}\text{O}_5, 2\text{H}_2\text{SO}_4$ , when treated in the cold with a mixture of acetic and strong sulphuric acids. On addition of water (in small quantities) to the mixture of fluorescein and the acetic and sulphuric acids, a yellow powder was obtained :

0.3858 gave 0.2044  $\text{BaSO}_4$ .  $\text{SO}_4 = 22.05$ .

$\text{C}_{20}\text{H}_{12}\text{O}_5, \text{H}_2\text{SO}_4$  requires  $\text{SO}_4 = 22.33$  per cent.

*Fluorescein Disulphate*,  $\text{C}_{20}\text{H}_{12}\text{O}_5, 2\text{H}_2\text{SO}_4$ , forms microscopic, light yellow prisms :

0.2740 gave 0.2315  $\text{BaSO}_4$ .  $\text{SO}_4 = 34.81$ .

0.3444 „ 0.2882  $\text{BaSO}_4$ .  $\text{SO}_4 = 34.48$ .

$\text{C}_{20}\text{H}_{12}\text{O}_5, 2\text{H}_2\text{SO}_4$  requires  $\text{SO}_4 = 36.36$  per cent.

Part of the expense incurred in carrying out these experiments was defrayed by a grant received from the Government Grant Committee of the Royal Society.

EAST LONDON TECHNICAL COLLEGE.

## LXX.—Action of Hydrogen Peroxide on Carbohydrates in the Presence of Ferrous Sulphate. III.

By ROBERT SELBY MORRELL and JAMES MURRAY CROFTS.

THE specific action of hydrogen peroxide in the presence of ferrous sulphate was first demonstrated by Fenton in the oxidation of tartaric acid to dihydroxymaleic acid (*Trans.*, 1894, 65, 899), and later in the oxidation of polyhydric alcohols to aldoses (Fenton and Jackson, *Trans.*, 1899, 75, 1). Cross, Bevan, and Smith (*Trans.*, 1898, 73, 500) have investigated the action of these two reagents on dextrose, and found that in addition to tartaric acid a substance was formed which gave an im-

mediate precipitate with phenylhydrazine acetate, but they were unable to decide the nature of the substance. In communication with these authors, we have continued the investigation, and have shown that dextrose, lævulose, arabinose, and rhamnose are transformed by this peculiar action of hydrogen peroxide in the presence of ferrous sulphate into osones, which were recognised by their power to react with substituted hydrazines at the ordinary temperature, yielding osazones (Trans., 1899, 75, 787; 1900, 77, 1219).

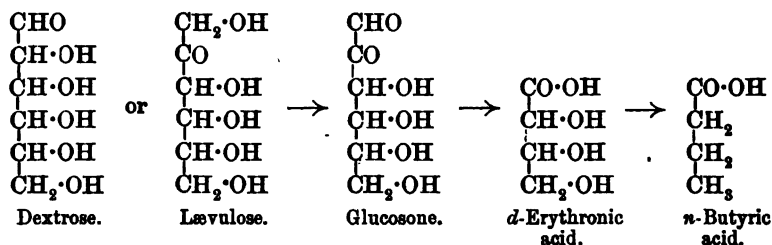
Mannose and galactose on oxidation would be expected to yield osones. In the case of mannose, an osone is formed giving, with phenylhydrazine, phenylglucosazone, but galactose behaves differently, and we are unable as yet to determine to what extent this sugar is oxidised by hydrogen peroxide in the presence of ferrous sulphate.

Fischer (*Ber.*, 1894, 27, 2031) states that galactose and *d*-talose are acted on by ferments with greater difficulty than dextrose and mannose, and in explanation of this difference he refers to the arrangement of the CH·OH groups, which in galactose and *d*-talose is very unlike that in dextrose and mannose. We consider that the internal compensating positions of the hydrogen atoms and hydroxyl groups may account for galactose behaving differently from other hexoses when oxidised by hydrogen peroxide in the presence of ferrous sulphate. We have attempted the preparation of glucosone from dextrose and lævulose, and have obtained a white, amorphous solid which gave analytical numbers agreeing with those required for the formula  $C_6H_{12}O_6$  or  $C_6H_{10}O_6$ ; it is not easy to decide between the two formulæ from the percentages of carbon and hydrogen. The white solid reacted immediately with phenylhydrazine acetate at the ordinary temperature and gave a good yield of phenylglucosazone. From its optical activity, we are led to the conclusion that it was contaminated with a small quantity of the parent carbohydrate, since the osone obtained from dextrose was slightly dextrorotatory, whilst the osone from lævulose had a lævorotatory power less than that of lævulose. Glucosone, obtained from phenylglucosazone by E. Fischer, is feebly lævorotatory (*Ber.*, 1889, 22, 89).

We have fermented solutions of glucosone from dextrose and lævulose and found that at the end of the fermentation the solution was slightly lævorotatory and still reacted immediately with phenylhydrazine acetate.

In order to test further the truth of the statement that osones are formed when carbohydrates are oxidised under the conditions given above, we have tried the action of bromine on aqueous solutions of glucosone obtained from dextrose and lævulose and have obtained good yields of salts of an acid which is not gluconic acid, but trihydroxybutyric acid identical with that obtained from erythritol by oxidation

with nitric acid (Lamparter, *Annalen*, 1865, 134, 260), or from *d*-erythrose by the action of bromine (Ruff, *Ber.*, 1899, 32, 3678). The barium and calcium salts of *d*-erythronic acid, obtained from dextrose or lævulose, have been reduced with hydriodic acid and phosphorus, and gave *n*-butyric acid which was easily identified by means of its silver salt. It has not been shown, so far as we know, that trihydroxybutyric acid is an oxidation product of dextrose, although Iwig and Hecht (*Ber.*, 1886, 19, 169) have obtained a trihydroxybutyric acid in small quantities from mannitol by oxidation with potassium permanganate. Trihydroxybutyric acid has also been obtained from lævulose by the action of mercuric oxide and baryta, or by the action of bromine (Börnstein and Herzfeld, *Ber.*, 1886, 18, 3354; Herzfeld, *Annalen*, 1888, 244, 291; Ruff, *Ber.*, 1899, 32, 3680). Ruff states that the yield of trihydroxybutyric acid obtained from lævulose is exceedingly small, but he was able to prepare a brucine salt of this acid which was identical with the brucine salt of *d*-erythronic acid. We have found that the amount of calcium trihydroxybutyrate obtained from lævulose by the direct action of bromine was not more than 1 per cent. of the weight of the lævulose taken. The transformation of dextrose and lævulose into glucosone, trihydroxybutyric acid (*d*-erythronic acid), and into *n*-butyric acid can be expressed in the following manner:



We are engaged on the further investigation of the properties of osones obtained by the action of hydrogen peroxide on carbohydrates in the presence of ferrous salts, and hope to communicate at an early date the results of the action of bromine on a solution of rhamnosone which would point to the formation of a methylglyceric acid—a result which may have an important bearing on the constitution of rhamnose.

#### EXPERIMENTAL.

##### *Oxidation of Mannose.*

Forty grams of seminose syrup were transformed into mannose hydrazone by treatment with phenylhydrazine acetate. The hydrazone was decomposed by benzaldehyde and the purified mannose obtained as a syrup, which was found to contain about 8 grams of the

sugar. One hundred and fifty c.c. of a 5 per cent. solution of mannose were treated with hydrogen peroxide of 20-volume strength in the presence of 1 gram of ferrous sulphate. The amount of hydrogen peroxide used was such as to yield 0.66 gram of oxygen, which was the calculated quantity required for the transformation of 7.5 grams of mannose into its osone. The oxidiser was added slowly in tenths of the required quantity, as in the oxidation of dextrose and lævulose. An aqueous solution of the osone was obtained in the manner described in a former paper (Trans., 1900, 77, 1219). On treatment of the solution of the osone with phenylhydrazine at the ordinary temperature, a yellow precipitate formed immediately. After being allowed to stand for a few hours, the precipitate was filtered, washed with alcohol and ether, and dried in a vacuum. The yield of glucosazone was 5 grams. On recrystallisation from alcohol, the glucosazone melted at  $204^{\circ}$  with decomposition and gave the following numbers on analysis :

0.1670 gave 0.3789  $\text{CO}_2$  and 0.1017  $\text{H}_2\text{O}$ . C = 60.1 ; H = 6.6.

0.0678 ,, 9.1 c.c. moist nitrogen at  $12^{\circ}$  and 750 mm. N = 15.68.

$\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_4$  requires C = 60.3 ; H = 6.2 ; N = 15.65 per cent.

Twenty grams of semiose, which had not been purified by the method given above, yielded, after oxidation with hydrogen peroxide in the presence of ferrous sulphate, 4 grams of glucosazone, which, on recrystallisation, melted at  $199^{\circ}$  with decomposition and contained 15.98 per cent. of nitrogen.

#### *Preparation of Glucosone from Dextrose or Lævulose.*

An aqueous solution of glucosone, prepared from lævulose (Trans., 1900, 77, 1219), was concentrated to a syrup in a vacuum at  $50^{\circ}$ . The syrup was poured into warm absolute alcohol and the alcohol solution filtered and concentrated in a vacuum on the water-bath and finally poured into dry ether. A white, amorphous solid separated, which was dissolved in hot absolute alcohol and the solution, after filtration and concentration, poured into dry ether. The yield of the white, amorphous solid from 60 grams of lævulose amounted to 3 grams. An analysis of the substance dried in a vacuum gave the following numbers :

0.1782 gave 0.2608  $\text{CO}_2$  and 0.0949  $\text{H}_2\text{O}$ . C = 39.92 ; H = 5.87.

$\text{C}_6\text{H}_{10}\text{O}_6$  requires C = 40.40 ; H = 5.61 per cent.

The glucosone, which was practically free from ash, reduced Fehling's solution without being warmed.

Glucosone from dextrose was prepared in the same way, except that



hydrogen peroxide of 10-volume strength was used instead of 20-volume strength. An analysis of the substance dried in a vacuum showed it to be less pure than the glucosone obtained from lævulose:

0.2002 gave 0.2905  $\text{CO}_2$  and 0.1162  $\text{H}_2\text{O}$ .  $\text{C} = 39.57$ ;  $\text{H} = 6.4$ .

It was not free from impurity, since 0.2 gram of substance, after ignition, was found to contain 0.9 mg. of ash. The glucosone reduced Fehling's solution at the ordinary temperature. Both the samples of glucosone reacted immediately with a cold solution of phenylhydrazine acetate. One gram of glucosone from dextrose dissolved in 10 c.c. of water was treated with 2 grams of phenylhydrazine dissolved in 2 c.c. of 50 per cent. acetic acid and diluted with 4 c.c. of water. A precipitate was formed immediately. After standing for some hours at the ordinary temperature, the glucosazone was filtered off, washed with water, and dried in a vacuum. The weight of the osazone amounted to 0.5 gram. Half a gram of glucosone from lævulose dissolved in 70 c.c. of water and treated with 1 gram of phenylhydrazine in 50 per cent. acetic acid gave 0.23 gram of glucosazone. The liquid was kept quite cold, and under these conditions both dextrose and lævulose do not give a precipitate with phenylhydrazine acetate unless the solutions are allowed to stand for several days. On recrystallisation from alcohol, the osazone melted at  $203^\circ$  with decomposition, and its identity was further established by a nitrogen determination:

0.0653 gave 8.4 c.c. moist nitrogen at  $12^\circ$  and 760 mm.  $\text{N} = 15.2$ .

$\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_4$  requires  $\text{N} = 15.65$  per cent.

The determination of the optical activity of the glucosone from dextrose and lævulose gave results which were unsatisfactory, and we concluded that small quantities of the parent sugar were present as impurity, especially in the case of the glucosone from dextrose, for the preparation of which 10-volume hydrogen peroxide was used. The glucosone in each case was dissolved in water:

0.504 gram of glucosone from lævulose had  $[\alpha]_D - 54^\circ$ ;

0.5247 " " dextrose "  $[\alpha]_D + 13.5^\circ$ ; whereas

0.5154 " lævulose dissolved in water had  $[\alpha]_D - 89^\circ$ .

E. Fischer states that glucosone prepared from phenylglucosazone is feebly lævorotatory (*Ber.*, 1889, 22, 89).

We have fermented solutions of glucosone from dextrose and lævulose with yeast in order to remove these carbohydrates. A solution of glucosone from dextrose had a decided dextrorotatory power, but after two days' fermentation at  $30^\circ$  became feebly lævorotatory. The fermentation was continued for another day, but there was no change in the rotatory power. After the removal of the inorganic impurities by

concentration of the aqueous solution of the glucosone in a vacuum on the water-bath and treatment with absolute methyl alcohol, a syrup was obtained which did not crystallise, but reacted immediately with phenylhydrazine acetate at the ordinary temperature.

A solution of glucosone prepared from lævulose was treated in exactly the same manner. The lœvorotatory power became less on fermentation and after two days the fermentation stopped. The solution was found to be slightly lœvorotatory and reacted immediately with a cold solution of phenylhydrazine acetate.

*Oxidation of an Aqueous Solution of Glucosone prepared from Dextrose.*

An aqueous solution of glucosone prepared from 30 grams of dextrose was heated with 12.5 grams of bromine at 40° for 12 hours (the volume of the solution was 350 c.c.). The excess of bromine was removed by a current of air and the yellow liquid was treated with an excess of lead carbonate. After standing for 24 hours, the liquid was filtered from lead carbonate and lead bromide, and sulphuretted hydrogen was passed in. The filtrate from the lead sulphide was concentrated to a small bulk in a vacuum at 60° on the water-bath. It was found to be impossible to remove the last traces of hydrobromic acid by silver carbonate as the solution contained a reducing substance. The residual liquid was boiled with calcium carbonate until it was neutral, decolorised with animal charcoal, filtered, evaporated in a vacuum on the water-bath to a small bulk, and poured into absolute alcohol. The calcium salt was obtained as a granular precipitate which was washed with absolute alcohol and ether and the ether removed in a vacuum. The yield of the salt varied between 25 and 30 per cent. of the weight of dextrose taken. It was purified by treatment with the calculated quantity of oxalic acid, and after boiling with calcium carbonate and decolorising with animal charcoal was reprecipitated by absolute alcohol. The yield of the purified salt was never less than 12—15 per cent. of the weight of the dextrose used. Analysis of the calcium salt gave the following numbers :

0.1995, air dried, gave 0.2072  $\text{CO}_2$  and 0.0872  $\text{H}_2\text{O}$ . C = 28.38 ; H = 4.85.

0.1958 dried at 110° „ 0.223  $\text{CO}_2$  „ 0.0735  $\text{H}_2\text{O}$ . C = 31.0 ; H = 4.2.

0.4170 „ 110° gave 0.1785  $\text{CaSO}_4$ . Ca = 12.6.

0.315 „ 110—130° „ 0.1405  $\text{CaSO}_4$ . Ca = 13.1.

0.4253 of the air-dried salt „ 0.1602  $\text{CaSO}_4$ . Ca = 11.08.

$(\text{C}_4\text{H}_7\text{O}_5)_2\text{Ca}, 2\text{H}_2\text{O}$  requires Ca = 11.56 ; C = 27.74 ; H = 5.2 per cent.

$(\text{C}_4\text{H}_7\text{O}_5)_2\text{Ca}$  „ Ca = 12.9 ; C = 30.96 ; H = 4.5 „

These numbers show that the salt is most probably calcium trihydroxybutyrate,

*Lead Erythronate*,  $(C_4H_6O_5)_2Pb$ .—The lead salt was prepared by adding normal lead acetate to a solution of the purified calcium or barium salt. The white precipitate so obtained was well washed with hot water, and after being dried at  $130^\circ$  was analysed:

0.1628 gave 0.1448  $PbSO_4$ .  $Pb = 60.8$ .

0.1550 „ 0.1660  $PbSO_4$ .  $Pb = 60.8$ .

$(C_4H_6O_5)_2Pb$  requires  $Pb = 60.7$  per cent.

This salt was obtained by Lamparter from erythronic acid (*loc. cit.*), and is insoluble in dilute acetic acid. It has been considered to be a characteristic salt of *n*-trihydroxybutyric acid (Fischer, *Ber.*, 1889, 22, 110; Fenton, *Trans.*, 1899, 75, 7). The lead salt obtained by us was insoluble in dilute acetic acid.

*Barium Erythronate*,  $Ba(C_4H_7O_5)_2 \cdot 2H_2O$ .—For the analysis, the barium salt obtained by boiling the solution containing erythronic acid with barium carbonate and precipitating with alcohol must be freed from iron compounds, which are present in small quantity. This was done by dissolving the barium salt in a small volume of water, adding alcohol in slight excess, filtering, and washing the undissolved residue, which was brown in colour, with a little cold water. The filtrate contained the barium erythronate, which was treated with dilute sulphuric acid, the liquid boiled with barium carbonate, and the pure barium salt reprecipitated by alcohol. On analysis:

0.1803 lost, at  $130^\circ$ , 0.01450  $H_2O$ .  $H_2O = 8.04$ .

0.1653, dried at  $130^\circ$ , gave 0.0938  $BaSO_4$ .  $Ba = 33.31$ .

0.1645, „ „ 0.0943  $BaSO_4$ .  $Ba = 33.76$ .

$Ba(C_4H_7O_5)_2 \cdot 2H_2O$  requires  $H_2O = 8.03$  per cent.

$Ba(C_4H_7O_5)_2$  „  $Ba = 33.66$  „

*Reduction of Calcium Erythronate to Butyric Acid*.—Fifteen grams of calcium erythronate, obtained from dextrose, were heated for 8 hours with 130 c.c. of hydriodic acid (b. p.  $127^\circ$ ) and 5 grams of amorphous phosphorus in a flask fitted with a reflux condenser on a sand-bath. The brown liquid was diluted with an equal volume of water and shaken six times with ether. The ether was distilled off and a brown oil was left which possessed a strong odour of butyric acid. To complete the reduction, the oil was heated with dilute sulphuric acid and zinc for an hour in a flask fitted with a reflux condenser. After being allowed to stand for several hours, the excess of zinc was filtered off and a little more sulphuric acid was added to the filtrate. A current of steam was passed into the liquid and the distillate, which was strongly acid, was neutralised with calcium carbonate. After filtration and concentration on the water-bath, 1.2 grams of a salt crystallised out. This salt had the characteristic properties of

calcium butyrate, being less soluble in hot water than in cold, and having the peculiar odour of the acid. To confirm the formation of butyric acid, the silver salt was prepared from the calcium salt, dried in a vacuum, and analysed :

0.2345 gave 0.1345 Ag.  $\text{Ag} = 55.4$ .

0.1708 „ 0.0948 Ag.  $\text{Ag} = 55.5$ .

$\text{C}_4\text{H}_7\text{O}_2\text{Ag}$  requires  $\text{Ag} = 55.4$  per cent.

The total yield of calcium butyrate from 15 grams of calcium erythronate was about 15 per cent. of the theoretical amount.

*Oxidation of an Aqueous Solution of Glucosone prepared from Lævulose.*

The action of bromine on an aqueous solution of glucosone prepared from lævulose was exactly the same as in the case of glucosone obtained from dextrose, and it is unnecessary to repeat the details of the separation and purification of the calcium or barium erythronate. From 30 grams of lævulose in each case, the yield of calcium salt amounted to 15 grams or, 50 per cent. of the theoretical, and of barium salt to 11 grams, or 30 per cent. of the theoretical.

The calcium salt, dried at  $110^\circ$ , was analysed :

0.2050 gave 0.2360  $\text{CO}_2$  and 0.0845  $\text{H}_2\text{O}$ .  $\text{C} = 31.3$  ;  $\text{H} = 4.6$ .

0.2875 „ 0.1285  $\text{CaSO}_4$ .  $\text{Ca} = 13.15$ .

0.2875 „ 0.1280  $\text{CaSO}_4$ .  $\text{Ca} = 13.1$ .

$(\text{C}_4\text{H}_7\text{O}_5)_2\text{Ca}$  requires  $\text{C} = 31.0$  ;  $\text{H} = 4.5$  ;  $\text{Ca} = 12.9$  per cent.

The barium salt, dried at  $130^\circ$ , was analysed, with the following results :

0.2255 lost 0.0190  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 8.4$ .

0.2065 gave 0.1195  $\text{BaSO}_4$ .  $\text{Ba} = 33.8$ .

$(\text{C}_4\text{H}_7\text{O}_5)_2\text{Ba} \cdot 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 8.0$  per cent.

$(\text{C}_4\text{H}_7\text{O}_5)_2\text{Ba}$  „  $\text{Ba} = 33.66$  „

The lead salt of erythronic acid was prepared from the barium salt. The yield amounted to 1 gram from 3 grams of barium salt, that is, about 25 per cent. of the calculated quantity :

0.1648, dried at  $130^\circ$ , gave 0.1465  $\text{PbSO}_4$ .  $\text{Pb} = 60.5$ .

$(\text{C}_4\text{H}_6\text{O}_5)_2\text{Pb}$  requires  $\text{Pb} = 60.77$  per cent.

It is not necessary to dry the salt at so high a temperature as  $160^\circ$  (Lamparter, *loc. cit.*).

*Strychnine Salt.*—When the calcium salt was treated with the calculated quantity of oxalic acid and any excess of oxalic acid removed by lime water, a solution of the free acid was obtained, which, on concentration, yielded a syrup which did not crystallise. From the

solution of the acid, by boiling with strychnine, filtering and concentrating, and treating with absolute alcohol, the strychnine salt was precipitated, which, after recrystallising twice from a small quantity of water, gave, on analysis, the following numbers :

0.1777, dried at  $130^{\circ}$ , gave 0.4137  $\text{CO}_2$  and 0.0985  $\text{H}_2\text{O}$ .  $\text{C} = 63.6$ ;  $\text{H} = 6.1$ .  
 0.1818, dried in a desiccator, gave 0.4083  $\text{CO}_2$  and 0.0185  $\text{H}_2\text{O}$ .  $\text{C} = 61.24$ ;  
 $\text{H} = 6.57$ .

$\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2, \text{C}_4\text{H}_8\text{O}_5$  requires  $\text{C} = 63.8$  ;  $\text{H} = 6.15$  per cent.  
 $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2, \text{C}_4\text{H}_8\text{O}_5, \text{H}_2\text{O}$  "  $\text{C} = 61.47$  ;  $\text{H} = 6.55$  "

The strychnine salt crystallised in needles from water, and contained one mol. of water of crystallisation which was not expelled under  $130^{\circ}$ .

*Reduction of Erythronic Acid, obtained from Levulose, to Butyric Acid.*—The details of this reduction are identical with those described under the reduction of calcium erythronate from dextrose. The yield of calcium or barium butyrate was about the same as in the reduction of the calcium salt from dextrose. The calcium or barium butyrate was transformed into the silver salt, which crystallised from water in white needles.

The *silver* salt was analysed :

0.1814 gave 0.1003 Ag.  $\text{Ag} = 55.3$ .  
 $\text{C}_4\text{H}_7\text{O}_2\text{Ag}$  requires  $\text{Ag} = 55.4$  per cent.

#### *Oxidation of Erythritol by Nitric Acid.*

Lamparter prepared erythronic acid from erythritol by the action of strong nitric acid on a hot concentrated aqueous solution of erythritol (*loc. cit.*). Przibytik (*J. Russ. Phys. Chem. Soc.*, 1881, 12, 208) states that dilute nitric acid transforms erythritol into oxalic acid and mesotartaric acid.

Ten grams of erythritol were oxidised by 25 c.c. of nitric acid of sp. gr. 1.2 at  $40^{\circ}$  for 28 hours, the liquid diluted with water, and the nitric acid removed by distillation in a vacuum at  $50^{\circ}$ . A syrup was obtained which contained oxalic and erythronic acid. The calcium erythronate was prepared in the usual way and precipitated by means of alcohol. The salt was purified by treatment with oxalic acid and calcium carbonate and was precipitated from its aqueous solution with alcohol, and washed with ether. The yield of the purified salt was 7.5 grams :

0.2432, dried at  $110^{\circ}$ , gave 0.1085  $\text{CaSO}_4$ .  $\text{Ca} = 13.1$ .  
 $(\text{C}_4\text{H}_7\text{O}_5)_2\text{Ca}$  requires  $\text{Ca} = 12.9$  per cent.

This salt is evidently identical with the calcium erythronate already

described, and from it a lead salt was obtained insoluble in dilute acetic acid.

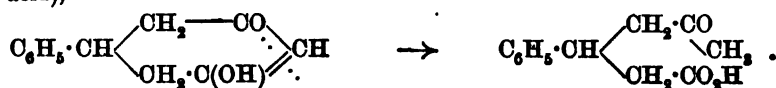
The authors desire to express their thanks to the Government Grant Committee of the Royal Society for funds which have enabled them to carry out this investigation.

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CAMBRIDGE.

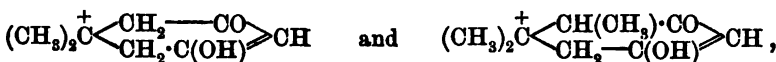
## LXXI.—*Preparation and Properties of 4-isoPropyl-dihydroresorcin.*

By ARTHUR WILLIAM CROSSLEY.

AMONG the many interesting changes which substituted dihydroresorcins undergo is one which they suffer on treatment with barium hydroxide. For example, Vorländer has shown (*Annalen*, 1897, 294, 317; 1899, 308, 188) that when 4-phenyldihydroresorcin is boiled with barium hydroxide, hydrolysis takes place and the ring is broken with formation of  $\beta$ -phenyl- $\delta$ -ketohectic acid ( $\beta$ -phenyl- $\gamma$ -acetylbutyric acid),



Exceptions are found to this reaction in the cases of 4:4-dimethyldihydroresorcin and 3:4:4-trimethyldihydroresorcin (compare *Ber.*, 1897, 30, 1801, and *Trans.*, 1901, 79, 139),

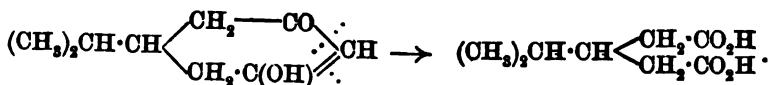


neither of which substances behaves in the above-mentioned manner. The explanation is evidently to be sought in a difference of constitution. These two substituted dihydroresorcins differ in one point, and one point only, from those which have been found to hydrolyse on treatment with barium hydroxide: they contain two alkyl groups attached to the same carbon atom (marked with a +), whereas all those which have been found to undergo hydrolysis contain only one alkyl group in this position.

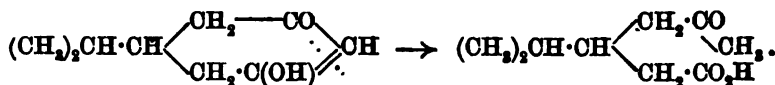
In order to obtain further evidence on this point, 4-*isopropyl*dihydroresorcin has been prepared, and its behaviour towards barium hydroxide investigated.

The starting point of the preparation was isobutylideneacetone,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_3$ , prepared according to the directions of Franke and Kohn (*Monatsh.*, 1899, 20, 876), and as this substance condenses with ethyl sodiomalonate to give *ethyl 4-isopropylidihydroresorcyate*,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}\begin{matrix} \text{CH}(\text{CO}_2\text{Et})\cdot\text{CO} \\ \text{CH}_2-\text{C}(\text{OH}) \end{matrix}\text{CH}$ , a characteristic reaction of  $\alpha\beta$ -unsaturated ketone, it affords a further proof, if such were needed, of the formula assigned to this ketone by Franke and Kohn.

When the above ethyl salt is hydrolysed with either sodium carbonate or potassium hydroxide, 4-isopropylidihydroresorcin (formula I below) is obtained, which crystallines with  $1\text{H}_2\text{O}$ . Its constitution is proved by its method of formation, and also by the fact that on oxidation with sodium hypobromite it gives rise to  $\beta$ -isopropylglutaric acid (compare *Trans.*, 1899, 75, 772; 1901, 79, 139):

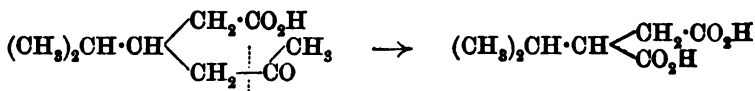


When boiled with barium hydroxide solution, isopropylidihydroresorcin is hydrolysed, as expected, with production of  $\beta$ -isopropyl- $\delta$ -ketohezoic acid:



Apparently, then, it is the presence of two alkyl groups attached to one and the same carbon atom which differentiates between substituted dihydroresorcins hydrolysed by barium hydroxide and those which are not.

The ketonic nature of isopropylketohezoic acid was proved by the preparation from it of a semicarbazide and an oxime; and its constitution follows from the oxidation with dilute nitric acid, when it yields pimelic (isopropylsuccinic) acid,

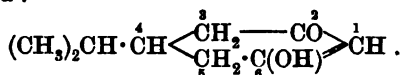


whereas isopropylidihydroresorcin, under similar conditions, gives  $\beta$ -isopropylglutaric acid.

The following comparison of the properties of isopropylidihydroresorcin and isopropylketohezoic acid leaves no doubt as to the non-identity of the two substances:

	M. p. or b. p.	Fe <sub>2</sub> Cl <sub>6</sub> .	Water.	Oxidation product.	M. p. of oxime.
4'-isoPropyldihydro- resorcin .....	82° 187° under 15 mm.	{ Violet colour. No colour.	C <sub>9</sub> H <sub>14</sub> O <sub>2</sub> .H <sub>2</sub> O m. p. 67·5°. Appreciably soluble.	isoPropylglutaric acid .....	145° 93—94°
β-isoPropyl-δ-keto- hexoic acid .....				isoPropylsuccinic acid .....	

In previous communications (Trans., 1901, 79, 138; Proc., 1901, 17, 172), substituted dihydroresorcins have been called substituted dihydroresorcinols or diketocyclohexanes; but the author no longer retains these latter names, for although the substances behave apparently as diketones towards hydroxylamine, there can be no doubt that their most usual form is the ketoenolic constitution, represented by the following formula:

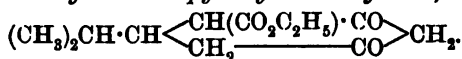


The positions of the various substituting groups are indicated by numbering the carbon atoms as above.

For these reasons, and also for brevity's sake, the name dihydroresorcin will in future be adopted to designate this class of substances.

#### EXPERIMENTAL.

*Ethyl 4-isoPropyldihydroresorcyate-3,*



Twenty-three grams of sodium were dissolved in 275 c.c. of absolute alcohol, 170 grams of ethyl malonate added, and, after cooling, 112 grams of isobutylideneacetone (Franke and Kohn, *Monatsh.*, 1899, 20, 876). The mixture became reddish-pink and much heat was evolved. On shaking, the whole set to a faintly-yellow, semi-solid mass, which was heated on the water-bath for 4 hours to complete the reaction; water was then added, the alcohol evaporated, and the alkaline liquid extracted with ether, which treatment removes some unaltered material. After acidification with dilute sulphuric acid, the whole was again extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and the ether evaporated, when 230 grams of a thick, yellow liquid were obtained, which, on standing, became semi-solid. The mass was spread on porous earthenware, thus giving 100 grams of a white solid, and on extracting the porous plate with ether, 98 grams of a thick, yellow liquid were obtained, which



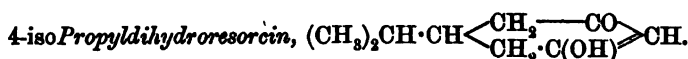
showed no signs of crystallisation after many months' standing, and is at present being more fully investigated.

The white solid was purified by crystallisation from a mixture of benzene and light petroleum, and analysed :

0.1107 gave 0.2572 CO<sub>2</sub> and 0.0804 H<sub>2</sub>O. C = 63.37 ; H = 8.07.

C<sub>12</sub>H<sub>18</sub>O<sub>4</sub> requires C = 63.71 ; H = 7.96 per cent.

Ethyl *isopropyl*dihydroresorcyate dissolves slightly in water and readily in the ordinary organic solvents. It crystallises from the above-mentioned mixture in stellar aggregates of small needles melting at 100.5–101°. Its aqueous solution gives a deep violet colour with ferric chloride solution.



Ethyl *isopropyl*dihydroresorcyate was hydrolysed by boiling for 2 hours with an equal weight of pure caustic potash dissolved in alcohol. (Hydrolysis may also be effected by boiling for about 15 hours with sodium carbonate solution.) Water was then added, the alcohol evaporated, and, after acidification with sulphuric acid, the whole extracted with ether and the ether evaporated. As this substituted dihydroresorcin crystallises with 1H<sub>2</sub>O, it is of advantage not to dry the ethereal solution before evaporation. The solid residue, obtained in nearly theoretical yield, was purified by crystallisation from dilute methyl alcohol and analysed :

0.1446 gave 0.3315 CO<sub>2</sub> and 0.1214 H<sub>2</sub>O. C = 62.52 ; H = 9.33.

C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>·H<sub>2</sub>O requires C = 62.79 ; H = 9.30 per cent.

*isoPropyl*dihydroresorcin is sparingly soluble in water or light petroleum, but readily so in the ordinary organic solvents ; its aqueous solution is intensely acid towards litmus paper and gives a deep purple colour with ferric chloride. It crystallises from dilute methyl alcohol, with 1H<sub>2</sub>O, in stout, flattened needles melting at 67.5°. When dried in a vacuum over sulphuric acid :

0.8860 lost 0.0940 H<sub>2</sub>O. H<sub>2</sub>O = 10.61.

C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>·H<sub>2</sub>O requires H<sub>2</sub>O = 10.46 per cent.

The dried substance, when heated in a capillary tube, melts at 82°, and at about 100° a red film is formed above the substance, a phenomenon noticed in the case of 4:4-dimethyldihydroresorcin (Trans., 1899, 75, 773). On analysis of the dried substance, the following numbers were obtained :

0.1197 gave 0.3073 CO<sub>2</sub> and 0.0980 H<sub>2</sub>O. C = 70.01 ; H = 9.10.

C<sub>9</sub>H<sub>14</sub>O<sub>2</sub> requires C = 70.13 ; H = 9.09 per cent.

The *silver* salt,  $C_9H_{13}O_3Ag$ , prepared in the usual manner, is a white, insoluble precipitate:

0.1761 gave 0.0727 Ag.  $Ag = 41.28$ .

$C_9H_{13}O_3Ag$  requires  $Ag = 41.38$  per cent.

The *dioxime* was obtained by adding the calculated quantities of hydroxylamine hydrochloride and sodium hydroxide dissolved in the smallest possible quantity of water to an alcoholic solution of the ketone. On standing, the solution became violet, and gradually deposited crystals, which were separated, purified by crystallisation from dilute methyl alcohol, and the nitrogen estimated:

0.1186 gave 15.6 c.c. moist nitrogen at  $16^\circ$  and 764 mm.  $N = 15.41$ .

$C_9H_{16}O_2N_2$  requires  $N = 15.22$  per cent.

The dioxime is insoluble in benzene or chloroform, but readily soluble in methyl or ethyl alcohol on warming, and crystallises from dilute methyl alcohol in clusters of stumpy needles. Its melting point is indefinite. On heating in a capillary tube, it runs together at  $145^\circ$ , forming a nearly clear jelly, which sticks to the side of the tube. On more strongly heating, it becomes cloudy, and at  $165^\circ$  decomposes and gives off gas.

The *ethyl ether*,  $C_8H_7 \cdot CH \begin{array}{c} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}_2 \cdot C(OC_2H_5) \end{array} \rangle CH$ , prepared by heating the dry silver salt with ethyl iodide in dry ethereal solution, is a clear, faintly yellow, oily liquid boiling at  $284^\circ$  at 762 mm.:

0.1204 gave 0.3190  $CO_2$  and 0.1086  $H_2O$ .  $C = 72.26$ ;  $H = 10.02$ .

$C_{11}H_{18}O_3$  requires  $C = 72.52$ ;  $H = 9.89$  per cent.

When hydrolysed with alcoholic potassium hydroxide, it is quantitatively reconverted into isopropylldihydroresorcin.

1-Bromo-4-isopropylldihydroresorcin,  $(CH_3)_2CH \cdot OH \begin{array}{c} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}_2 \cdot C(OH) \end{array} \rangle CBr$ , was prepared by adding a solution of bromine in chloroform to one of dried isopropylldihydroresorcin (m. p.  $82^\circ$ ) in chloroform until the colour of the former just remained permanent, when hydrogen bromide was evolved and a heavy oil separated, which soon solidified. This was filtered off, purified by crystallisation from dilute alcohol, and the bromine determined:

0.2076 gave 0.1692 AgBr.  $Br = 34.68$ .

$C_9H_{13}O_2Br$  requires  $Br = 34.33$  per cent.

Bromoisopropylldihydroresorcin is insoluble in water, readily soluble in alcohol, acetone, or ethyl acetate on warming, and crystallises in nacreous scales. Its melting point depends on the rate at which it is heated; when heated in the ordinary way, it melts sharply at  $169^\circ$  to a deep red liquid, which at once decomposes and gives off

gas. Other determinations in which the substance was heated more and more slowly gave 166°, 162°, and finally as low as 152°. In each case, the substance melted sharply at the given temperature with decomposition and evolution of gas.

*Oxidation of 4-isoPropyldihydroresorcin.*

I. *With Potassium Hypobromite.*—Thirty-four grams of bromine were poured into 400 c.c. of water cooled to 0° and a strong solution of sodium hydroxide slowly added until the colour of the bromine had disappeared. A solution of 7 grams of isopropyldihydroresorcin in sodium hydroxide (10 grams NaOH in 50 c.c. of water) was then poured in and the whole allowed to stand 4 hours. The solution, after separation from bromoform and carbon tetrabromide, was acidified with hydrochloric acid, evaporated to about one-fourth of its original bulk, and repeatedly extracted with ether. The ethereal solution, after drying over calcium chloride and evaporation of the ether, yielded 5 grams of a white solid, which proved to be  $\beta$ -isopropylglutaric acid (compare Howles, Thorpe, and Udall, Trans., 1900, 77, 942). Thus, it crystallised from water in stout needles melting at 100–100·5°, and gave a crystalline anilic acid melting at 121°. On analysis of the acid, the following numbers were obtained :

0·1422 gave 0·2861 CO<sub>2</sub> and 0·1028 H<sub>2</sub>O. C=54·87 ; H=8·03.

C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C=55·17 ; H=8·04 per cent.

II. *With Nitric Acid.*—Two grams of isopropyldihydroresorcin were heated to boiling with 20 c.c. of dilute nitric acid (1 : 1), when after a few moments oxidation took place vigorously. The whole was evaporated on the water-bath, with repeated addition of water, when 1·7 grams of a white solid were obtained melting at 100° and giving an anilic acid melting at 121°, thus proving it to be  $\beta$ -isopropylglutaric acid.

*$\beta$ -isoPropyl- $\delta$ -ketohezoic Acid*, CH<sub>3</sub>·CO·CH<sub>2</sub>·CH(C<sub>3</sub>H<sub>7</sub>)·CH<sub>2</sub>·CO<sub>2</sub>H.

isoPropyldihydroresorcin (1 part) was heated with barium hydroxide (4 parts) and water (20 parts) for 36 hours in a flask attached to a reflex condenser. The whole was then evaporated to about one-third of its original volume, acidified with hydrochloric acid, and extracted with ether. The ethereal solution, after drying over calcium chloride, was evaporated and the residual liquid purified by repeated distillation in a vacuum, and analysed :

0·1206 gave 0·2776 CO<sub>2</sub> and 0·1014 H<sub>2</sub>O. C=62·77 ; H=9·34.

C<sub>9</sub>H<sub>16</sub>O<sub>5</sub> requires C=62·79 ; H=9·30 per cent.

isoPropylketohezoic acid is a perfectly colourless, thick liquid with

a sharp, but not unpleasant odour. It boils at  $187^{\circ}$  under 15 mm. pressure, and requires to be distilled as rapidly as possible, for on slow distillation, especially in air, it decomposes. The *silver* salt,  $C_9H_{15}O_3Ag$ , prepared in the usual way, is a white, insoluble precipitate :

0.2184 gave 0.0852 Ag.  $Ag = 39.01$ .

$C_9H_{15}O_3Ag$  requires  $Ag = 38.71$  per cent.

The *semicarbazide*,  $C_{10}H_{19}O_3N_3$ , was obtained by adding to an alcoholic solution of the ketonic acid the calculated quantities of semicarbazide hydrochloride and sodium acetate dissolved in the smallest possible quantities of water and allowing the alcohol to evaporate slowly. The solid which separated crystallised from dilute alcohol in small, transparent plates melting at  $144^{\circ}$  with slow evolution of gas :

0.1146 gave 18.4 c.c. moist nitrogen at  $18^{\circ}$  and 756 mm.  $N = 18.44$ .

$C_{10}H_{19}O_3N_3$  requires  $N = 18.34$  per cent.

*Oxime*.—Five grams of hydroxylamine hydrochloride and 3 grams of sodium hydroxide dissolved in the smallest possible amount of water were added to an alcoholic solution of 5 grams of the ketonic acid and the solution heated to boiling for 4 hours. The pasty mass left on evaporating the solvent was warmed with absolute alcohol, filtered from sodium chloride, and the alcohol again evaporated. On stirring the residue with a few drops of very dilute acetic acid, it gradually solidified. It was spread on a porous plate, purified by crystallisation from ethyl acetate, and the nitrogen determined :

0.2064 gave 13.5 c.c. moist nitrogen at  $19.5^{\circ}$  and 755 mm.  $N = 7.45$ .

$C_9H_{17}O_3N$  requires  $N = 7.49$  per cent.

The oxime crystallises slowly in stellar aggregates of compact needles melting at  $93-94^{\circ}$ . It is practically insoluble in light petroleum, but ready soluble in the ordinary organic solvents, especially on warming.

*Oxidation of Acetylisopropylbutyric Acid*.—8.5 grams of the ketonic acid were heated with 90 c.c. of nitric acid (sp. gr. 1.15) for half an hour in a flask attached to a reflux condenser. The oxidation is not a very violent one. After adding water and evaporating off the nitric acid, 6 grams (calc., 7.3 grams) of a white solid were obtained, which crystallised from water in stout, transparent needles melting at  $115-116^{\circ}$ . This is the melting point of pimelic (*isopropylsuccinic*) acid (compare *Trans.*, 1898, 73, 22). To prove further the identity of this acid, a portion was converted into the silver salt, and analysed :

0.2598 gave 0.1498 Ag.  $Ag = 57.66$ .

$C_7H_{10}O_4Ag_2$  requires  $Ag = 57.75$  per cent.

The acid also gave an anhydride boiling at  $255^{\circ}$  at ordinary atmospheric pressure, and from this an *anilic acid* crystallising from dilute alcohol in shining scales melting at  $135^{\circ}$ .

As *isopropylsuccinanilic acid* does not appear to have been previously described, a specimen was made for comparison. The pimelic acid employed was obtained by the fusion of camphoric acid with potassium hydroxide (Trans., 1898, 73, 22). It was first converted into the anhydride boiling at  $255^{\circ}$  under ordinary atmospheric pressure, and this, on treatment with aniline in benzene solution, gave the anilic acid, crystallising from dilute alcohol in beautiful, nacreous scales melting at  $135^{\circ}$ . It is fairly soluble in benzene and chloroform on warming, and readily so in ether, ethyl acetate, acetone, or alcohol in the cold:

0.3006 gave 15.4 c.c. moist nitrogen at  $20^{\circ}$  and 766 mm.  $N = 5.91$ .

$C_{13}H_{17}O_3N$  requires  $N = 5.95$  per cent.

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant defraying the cost of the materials used in this investigation.

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## LXXII.—*The Influence of Temperature on Association in Benzene Solution, and the Value of the Molecular Rise of Boiling Point for Benzene at Different Temperatures.*

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SUBSTANCES containing hydroxyl groups give, as is well known, abnormal molecular weights in hydrocarbon solutions by both the cryoscopic and ebullioscopic methods. A large number of hydroxyl compounds have been investigated in benzene by Beckmann, Auwers, Paternò, and others, and it has been shown that they may be divided into two classes according to their behaviour with increasing concentration: carboxylic acids and oximes have in general the normal molecular weight in dilute solution; as the concentration is increased, the molecular weight increases, at first rapidly, then more slowly, until it reaches double the normal value; further increase of concentration affects the value but little. Alcohols and phenols also give the normal

molecular weight in dilute solutions, but the molecular weight found increases regularly with the concentration and does not seem to reach a limit. The behaviour of acids and oximes with increasing concentration is qualitatively similar to that of an associating gas such as  $\text{NO}_2$  when its pressure is increased, and in some cases the association follows Guldberg and Waage's law with sufficient closeness, in others the agreement is not satisfactory. It is generally assumed that the apparent increase in molecular weight in the case of the alcohols and phenols is due also to association taking place with increasing concentration.

Although the influence of concentration on association has been largely investigated, the effect of temperature has not, as yet, been measured. Molecular weight determinations have been carried out with a few substances by both the boiling and freezing point methods in benzene solution, and it might be assumed that the difference between the values found is due to the difference of temperature. It has yet to be shown that the increase in cryoscopic molecular weight is not due, in part, to separation of dissolved substance with the solid benzene. Until this has been done, it is not justifiable to compare the results of the two methods in the case of the alcohols and phenols. As most of the acids give almost the same molecular weight over a considerable range of concentration, the results obtained in this way with them are more trustworthy.

Several methods might be used to determine the influence of temperature on association in solution, the most promising being the variation of vapour pressure with temperature, and the boiling point method at different pressures. The latter method was chosen in the present research, partly because it has been more fully worked out, and partly to elucidate some other points about the boiling point method.

The value of the molecular rise of boiling point may be calculated in a number of ways. Arrhenius has shown that it may be calculated from the heat of vaporisation,  $100\tau = RT^2/L$ , where  $R$  is the gas constant,  $L$  the heat of vaporisation of one gram of the solvent, and  $T$  the absolute temperature. The total heat of vaporisation of benzene has been determined by Regnault (*Memoires de l'Institut*, 26, 881), and Schiff (*Annalen*, 1888, 244, 344) has determined the specific heat at different temperatures. The heat of vaporisation of benzene was calculated by means of their formulæ at intervals of  $10^\circ$ , and the values so obtained substituted in van't Hoff's equation.

By means of the latent heat equation, we can substitute  $L$  in  $100\tau = RT^2/L$ ; we thus obtain  $100\tau = Mp/(dp/dt)$  (Nernst and Roloff, *Zeit. physikal. Chem.*, 1893, 11, 24).

The same formula may be derived from the lowering of vapour

pressure equation,  $p - p'/p = n/N$  (Ostwald, *Grundriss*, 203, 1899 edition). The equation,  $100\tau = Mp/(dp/dt)$ , enables us to calculate the molecular rise of boiling point from the rate of change of vapour pressure with temperature, provided the substance has the normal molecular weight in the state of vapour at the boiling point, and the method is quite independent of the state of association of the liquid solvent.

The molecular rise of boiling point at atmospheric pressure has been determined in this way for a large number of solvents by Beckmann and Fuchs (*Zeit. physikal. Chem.*, 1895, 18, 492). The results obtained show a satisfactory agreement with those obtained by the direct method.

In the present case, the value of the molecular rise of boiling point has been calculated from Ramsay and Young's determinations of the vapour pressure of benzene at different temperatures (Ramsay and Young, *Phil. Mag.*, 1887, [v], 23, 61; Young, *Trans.*, 1899, 55, 501). The results so obtained are compared with those of determinations of the rise of boiling point, using phenanthrene, benzophenone, and in three cases benzil as dissolved substances, at pressures ranging from 31 to 109 cm. The pressures were chosen so as to give differences of about  $10^\circ$  in the boiling point of the benzene.

Determinations were also carried out at various pressures with typical abnormal substances. The substances chosen had to be solids, as it would be exceedingly difficult to introduce a liquid into the apparatus without disturbing the pressure; it was also necessary that they should be easily soluble and have very little vapour pressure at the highest temperature used. Benzoic acid, *o*-bromobenzoic acid,  $\beta$ -benzilmonoxime, and dimethyl tartrate were the substances used. The value of the results with benzoic acid may be partly vitiated by its volatility.

### *The Method.*

In order to carry out the experiments, it was necessary to maintain a very constant pressure in the boiling point apparatus for a considerable time.

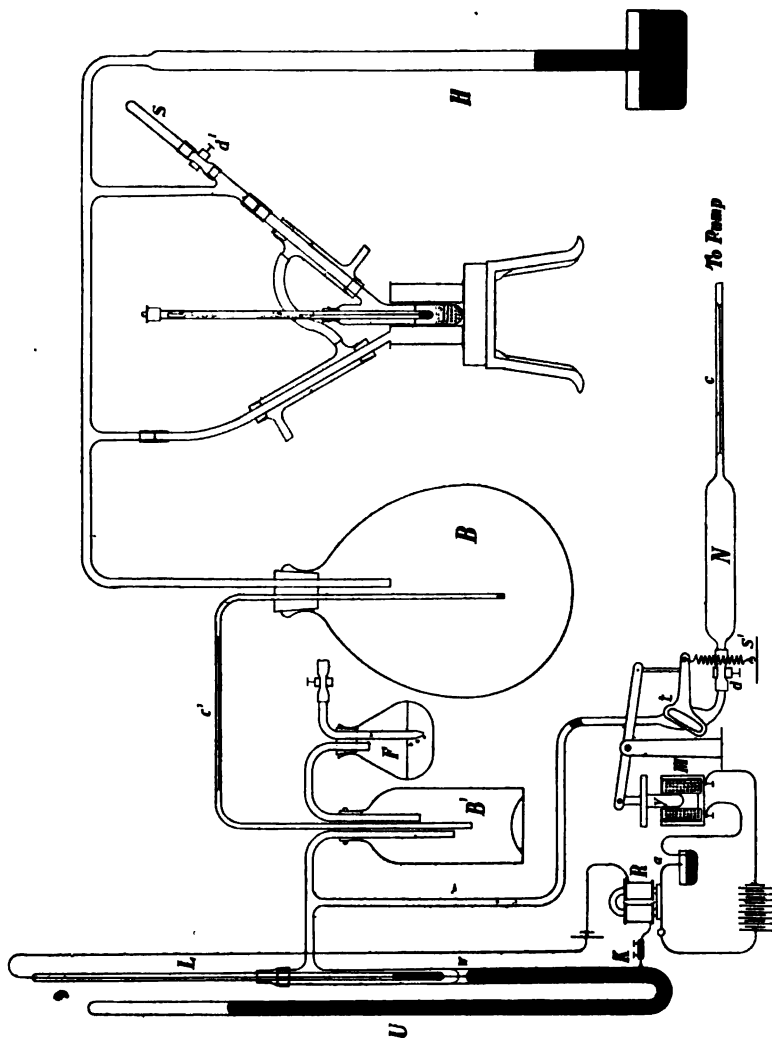
The arrangement of the apparatus,\* for pressures less than the atmospheric and its method of working will be readily understood on reference to Fig. 1.

The Beckmann apparatus is seen to the right; both the boiling point tube and the vapour mantle are connected to the large bottle, *B*, and the pressure in the apparatus may be found by reading the manometer,

\* An apparatus for maintaining a constant pressure near that of the atmosphere, similar in principle to that used, has been described by A. Smit (*Zeit. physikal. Chem.*, 1900, 38, 88).

*H*, and subtracting from the barometric height. The whole apparatus is connected with a water vacuum pump. *N* is a drying tube containing calcium chloride. The syphon barometer tube, *U*, has a platinum wire fused through at *K* and is connected to the pump through the

Fig. 1.



tap *t*. The tube *L* has a platinum wire fused through its lower end, *w*, electrical connection is made with the copper wire lead by a little mercury. Imagine the apparatus to be working and the tap to be open, the pressure in the apparatus falls and the mercury in the right



hand limb of  $U$  rises until it touches the platinum wire at  $w$ ; the circuit of the relay,  $R$ , is then complete and the arm,  $a$ , is raised, this breaks the circuit of the magnet,  $M$ , and the tap  $t$  is closed by the spring  $S'$ . Owing to leakage in the apparatus, the pressure gradually rises and the mercury falls until the contact at  $w$  is broken; the arm,  $a$ , then falls, completing the circuit of  $M$ , and the tap is opened. The pump was worked at its full power in all the experiments. To prevent too great a rush of air when the tap opened, a capillary tube,  $c$ , was placed between the pump and apparatus, and a final adjustment given to the rate at which the air was pumped out by the screw clip,  $d$ . It is evident that when the tap opens the pressure in  $U$  falls much more rapidly than in the bottle,  $B'$ , consequently the mercury rises and the tap is closed before the pressure in  $B'$  has time to fall much; the mercury in  $U$  then falls almost to its original height owing to equalisation of pressure in  $U$  and  $B'$ . The large bottle,  $B$ , was connected to  $B'$  by a capillary tube ( $c'$ ). The pressure in  $B$ , therefore, only follows the changes in  $B'$  slowly; it is obvious that if the pressure in  $B'$  varies rapidly by small amounts about a mean pressure, the pressure in  $B$  will be practically constant and will be the mean pressure in  $B'$ . The natural leakage in the apparatus was not sufficient to keep the tap opening and shutting quickly enough to give the most constant pressures; the whole apparatus was so tight that, working at 109 cm., the pressure only fell 2 cm. in an hour with the tap closed. A small flask,  $F$ , containing a little sulphuric acid was therefore connected to  $B'$ , and a stream of air, which could be regulated by means of a screw clip, allowed to bubble through the acid at a convenient rate. With the tap opening 20 to 30 times per minute, no motion at all could be observed, even with a magnifying telescope, in the mercury manometer,  $H$ ; using a water manometer for pressures near the atmospheric, only a slight motion, about  $1/5$  mm., was visible. To alter the pressure, the tube,  $L$ , is raised or lowered to the necessary amount. The tube slides in a piece of rubber pressure tubing and can easily be adjusted with sufficient accuracy in the required position. The surface of the mercury at  $W$  was covered with a little alcohol.

The magnet,  $M$ , was kindly designed for me by Dr. D. K. Morris so as to give as equal a pull as possible over a considerable range. An iron plug ( $y$ ) was connected to the keeper and this moved in the core of the magnet. The bottom and sides of the magnet were encased in iron. An ordinary glass tap was used for  $t$ , this was fitted, at a suitable angle, with a brass arm held on by plaster of paris.

The Beckmann boiling point apparatus was arranged in the usual way. A metal vapour jacket was used; this was about one-third filled with benzene. The boiling point tube and condenser were made in one piece, and the mouth of the boiling tube contracted so that a small

cork could be used. It, is of course, most important that there should be no leak in the boiling tube, as benzene would be swept out of it by the escaping air. A rubber stopper could not be used to hold the thermometer, as it was liable to absorb considerable quantities of benzene: a good, well softened cork was found to be perfectly tight. The loss of benzene after 3 or 4 hours seldom exceeded 0.1, and never 0.2 gram. The liquid in the boiling tube boiled quietly both under reduced and increased pressure, even the platinum wire usually fused through the bottom of the boiling tube was unnecessary. The beads were placed in the tube in the way described by the author (*Trans.*, 1901, 79, 261), and platinum clippings placed over them. The platinum cylinder was not used as the boiling temperatures were not high enough to make its use of advantage. The space between the boiling tube and vapour jacket was packed at top and bottom with asbestos paper. A gas regulator was used to keep the gas pressure constant. The flames were protected from draught by pieces of zinc fitting closely to the Beckmann stand, and the whole apparatus was surrounded by a zinc screen as high as the top of the boiling tube. An electrical tapper was used to tap the thermometer.

In the experiments at increased pressure, the capillary (c) was connected to a large metal reservoir into which air was forced by a large bicycle pump. A mercury manometer was in connection with the reservoir. The flask *F* was removed, and the delivery tube from *B'* joined to a tube drawn out to a point and dipping into water. The rate at which the air escaped could then be readily regulated by a screw clip. The relay was cut out and the leads from *U* connected directly to the large battery and *M*. It will be seen that the tap now opens when the pressure falls below that fixed upon and closes when it rises above it. The tap *t* was held in by a spring which pressed gently against it. It was found that more satisfactory results were obtained if the pressure in the air reservoir was kept considerably above that in the apparatus; an excess pressure of at least one-fourth of an atmosphere was used.

In the earlier experiments the pressure was allowed to vary considerably. In series (16) the pressure in the reservoir changed by about an atmosphere from time to time. In the other series at 79 cm. the variation was about one-fourth of an atmosphere. The experiments at 109 cm. were all carried out with a pressure in the reservoir which did not vary more than 2 cm. about the mean, and the thermometer readings were taken when the mercury in the manometer stood in the mean position. It will be seen that very concordant results were obtained, however much the pressure changed; the only reason for giving more attention to the pressure in the later experiments was that it seemed safer to work under as constant conditions as possible.

After the liquid had boiled about an hour, the temperature became as constant as it is at atmospheric pressure under favourable conditions.

When the temperature had become constant, the clip *d* was closed, the tube *S* removed, and the weighed pastille placed in it. The tube was then replaced, the clip removed, and *S* pushed well down into the rubber tube; on tapping gently, the substance fell into the boiling tube. The tube was then partly withdrawn and the clip replaced, when everything was ready for the addition of the next portion of substance. Working at increased pressures, the rubber tube was wired to *S* before the clip was opened, otherwise there was danger of *S* being blown out. As the rubber tube is fully distended in this case, the substance falls in without difficulty.

The benzene used in the experiments was carefully purified and was dried over sodium. The substances, with two exceptions, were purchased from Kahlbaum, and were pure. The  $\beta$ -benzilmonoxime was made according to Meyer and Auwers' instructions, and melted at  $113^{\circ}$  to  $114^{\circ}$ . The dimethyl tartrate was prepared by Frankland and Aston's method, and purified by distillation and precipitation from benzene by light petroleum.

The determinations at about  $80^{\circ}$  were carried out under atmospheric pressure.

*Determination of the Molecular Rise of Boiling Point at Different Temperatures.*

Column 1 gives the number of the series.

Column 2 „ the pressure in cm. at which the experiments were carried out.

Column 3 „ the corresponding temperature.

Column 4 „ the weight of solvent.

Column 5 „ the weight of substance.

Column 6 „ the observed rise of boiling point.

Column 7 „ grams of substance per 100 grams of solvent.

Column 8 „  $1/100$  gram-molecules of substance per 100 grams of solvent.

Column 9 „ the molecular rise of boiling point.

TABLE I.

1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>Diphenylamine</i> , $C_{12}H_{11}N = 169$ .								
1	24.4	48.0	21.55	0.2696 0.6984 1.692 2.458 3.384	0.139 0.365 0.840 1.270 1.678	1.28 3.29 7.53 11.62 16.0	0.754 1.95 4.45 6.88 9.47	18.4 18.7 19.6 19.2 18.4
							Mean...	19.0
<i>Phenanthrene</i> , $C_{14}H_{10} = 178$ .								
2	31.1	53.7	20.18	0.3040 0.706 1.270 1.989 3.127	0.184 0.427 0.755 1.165 1.789	1.54 3.57 6.42 10.06 15.8	0.863 2.00 3.61 5.65 7.05	21.3 21.3 20.9 20.6 20.1
							Mean...	21.0
3	31.7	54.3	19.81	0.2424 0.751 1.455 1.977 2.973	0.147 0.465 0.875 1.175 1.717	1.25 3.87 7.49 10.19 15.32	0.705 2.17 4.21 5.73 8.61	20.9 21.4 20.8 20.5 19.9
							Mean...	20.9
<i>Benzophenone</i> , $C_{13}H_{10}O = 182$ .								
4	31.0	53.7	21.31	0.2600 0.501 0.936 1.573 2.345 3.360	0.135 0.268 0.505 0.835 1.232 1.733	1.24 2.40 4.48 7.52 11.21 16.07	0.683 1.32 2.46 4.13 6.16 8.83	19.8 20.4 20.5 20.2 20.0 19.6
							Mean...	20.2
<i>Benzil</i> , $C_{14}H_{10}O_2 = 210$ .								
5	35.8	57.6	22.19	0.2794 0.454 0.771 1.157 1.702 2.401	0.128 0.211 0.357 0.534 0.774 1.063	1.28 2.08 3.53 5.30 7.81 11.03	0.611 0.99 1.68 2.53 3.72 5.24	21.0 21.3 21.2 21.1 20.8 20.3
							Mean...	21.0

TABLE I. (continued).

1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>Phenanthrene.</i>								
6	43.5	63.3	24.13	0.2320 0.5180 1.661 2.314 3.474 4.516	0.135 0.284 0.895 1.239 1.785 2.275	0.982 2.19 7.03 9.79 14.70 19.11	0.551 1.23 3.95 5.50 8.26 10.74	24.5 22.5 22.7 22.5 21.6 21.2
							Mean...	22.6
7	43.5	63.3	24.99	0.2240 0.4968 0.9260 1.546 2.477	0.112 0.258 0.472 0.787 1.240	0.910 2.02 3.76 6.29 10.07	0.512 1.13 2.11 3.53 5.65	21.9 22.7 22.3 22.3 21.9
							Mean...	22.22
<i>Benzophenone.</i>								
8	43.48	63.3	22.7	0.2450 0.5804 1.160 1.919 2.974 3.847	0.128 0.303 0.604 0.973 1.490 1.912	1.08 2.56 5.11 8.45 13.10 16.94	0.593 1.40 2.81 4.64 7.20 9.31	21.6 21.6 21.5 21.0 20.7 20.5
							Mean...	21.40
9	43.3	63.1	21.63	0.2914 0.7286 1.4308 2.163 3.226	0.170 0.406 0.793 1.171 1.703	1.37 3.43 6.94 10.16 15.18	0.754 1.89 3.71 5.47 8.35	22.6 21.5 21.4 21.4 20.4
							Mean...	21.72
<i>Phenanthrene.</i>								
10	60.3	72.8	22.19	0.2490 0.608 1.217 2.162 3.247 4.224	0.159 0.371 0.742 1.289 1.878 2.404	1.14 2.79 5.58 9.92 14.89 19.38	0.642 1.57 3.14 5.57 8.37 10.89	24.8 23.7 23.7 23.1 22.4 22.1
							Mean...	23.5

TABLE I. (continued).

1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>Phenanthrene</i> (continued).								
11	61.28	73.2	22.19	0.2230 0.4970 0.929 1.507 2.175 2.940	0.137 0.304 0.573 0.917 1.304 1.738	1.02 2.28 4.26 6.91 9.98 13.49	0.575 1.28 2.39 3.89 5.61 7.58	23.8 23.7 23.6 23.6 23.3 22.9
							Mean...	23.6
<i>Benzophenone.</i>								
12	61.3	73.2	22.19	0.3202 0.6920 1.182 1.946 2.723	0.174 0.401 0.681 1.130 1.563	1.47 3.18 5.42 8.93 12.49	0.807 1.74 2.98 4.91 6.87	21.6 23.0 22.8 23.0 22.8
							Mean...	22.95
<i>Phenanthrene.</i>								
13	75.7	80.2	22.19	0.1866 0.3884 0.6824 1.184 1.648 2.610	0.113 0.250 0.447 0.782 1.062 1.647	0.856 1.78 3.13 5.43 7.56 11.97	0.481 1.00 1.40 3.05 4.25 6.78	23.5 25.0 25.4 25.6 25.0 24.5
							Mean...	25.25
<i>Benzophenone.</i>								
14	75.3	80.0	22.19	0.3614 0.8166 1.2330 1.688 2.724	0.225 0.490 0.740 1.019 1.622	1.66 3.75 5.66 7.75 12.50	0.91 2.06 3.11 4.26 6.87	24.7 23.7 23.7 23.9 23.6
							Mean...	23.8

TABLE I. (*continued*).

1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>Benzil.</i>								
15	75.5	80.1	22.19	0.2556 0.5626 0.960 1.767 2.975 4.354	0.124 0.282 0.493 0.902 1.479 2.126	1.17 2.58 4.41 8.11 13.6 20.0	0.558 1.23 2.10 3.86 6.50 9.49	22.2 22.9 23.5 23.4 22.7 22.4
							Mean...	23.3
<i>Phenanthrene.</i>								
16	79.7	82.4	22.19	0.1836 0.3978 0.741 1.060 1.660 2.251	0.128 0.257 0.476 0.691 1.056 1.415	0.848 1.83 3.40 4.86 7.62 10.33	0.474 1.08 1.91 2.73 4.28 5.80	25.9 25.0 24.9 25.3 24.7 24.4
							Mean...	25.0
17	79.2	82.0	22.19	0.2094 0.4496 0.857 1.446 2.213 3.046 4.231	0.133 0.285 0.550 0.925 1.370 1.894 2.541	0.959 2.06 3.94 6.64 10.16 13.98 19.4	0.538 1.16 2.21 3.73 5.70 7.85 10.9	24.7 24.6 24.9 24.8 24.0 24.1 23.3
							Mean...	24.8
<i>Benzophenone.</i>								
18	79.2	82.0	22.19	0.2290 0.4706 0.767 1.165 1.672 2.488 3.327	0.135 0.273 0.446 0.669 0.967 1.403 1.894	1.05 2.16 3.52 5.35 7.67 11.4 15.3	0.577 1.19 1.93 2.94 4.22 6.27 8.39	23.4 23.0 23.1 22.8 22.9 22.4 22.6
							Mean...	23.0

TABLE I. (*continued*).

1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>Phenanthrene.</i>								
19	108.2	92.8	22.19	0.2800 0.5670 1.001 1.531 2.268 3.167 4.271	0.199 0.402 0.708 1.070 1.565 2.138 2.819	1.28 2.60 4.59 7.03 10.4 14.5 19.6	0.722 1.46 2.58 3.95 5.85 8.17 11.0	27.6 27.5 27.4 27.1 26.8 26.2 25.6
							Mean...	27.3
<i>Benzophenone.</i>								
20	109.0	93.1	22.19	0.2956 0.6452 1.076 1.599 2.169 2.871	0.197 0.427 0.717 1.073 1.405 1.843	1.86 2.96 4.94 7.34 9.95 13.2	0.745 1.63 2.71 4.03 5.47 7.24	26.4 26.3 26.4 26.6 25.7 25.5
							Mean...	26.4
<i>Benzil.</i>								
21	109.0	93.1	22.19	0.3026 0.613 0.998 1.548 2.556 3.613	0.184 0.352 0.579 0.876 1.403 1.940	1.39 2.81 4.58 7.10 11.7 16.6	0.661 1.34 2.18 3.38 5.58 7.90	27.8 26.3 26.6 25.9 25.1 24.6
							Mean...	26.2

The values of the molecular rise of boiling point given in the preceding tables, as well as the molecular weights to be given subsequently, are all calculated with 0.4 gram less solvent than was actually taken, to allow for the solvent adhering to the upper parts of the tube and for that in the state of vapour.

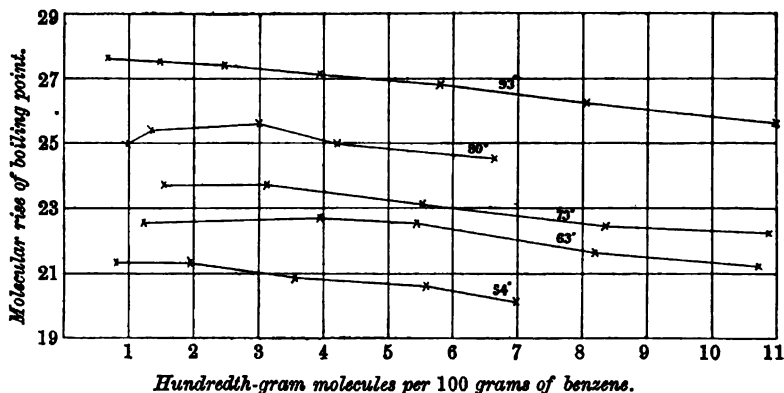
Three series of determinations were carried out with diphenylamine at 48°. Two of these gave values for  $\tau$  which rose or fell considerably with the concentration. The pump could only further reduce the pressure slowly, this may perhaps account for the error. All the experiments carried out, with the exception of the above-mentioned



series, and of two in which the tap failed to act for lack of sufficient grease, are given in the above tables.

On examination of the numbers, it will be noted that for concentrations of less than 6/100 gram-molecules per 100 grams of solvent, the

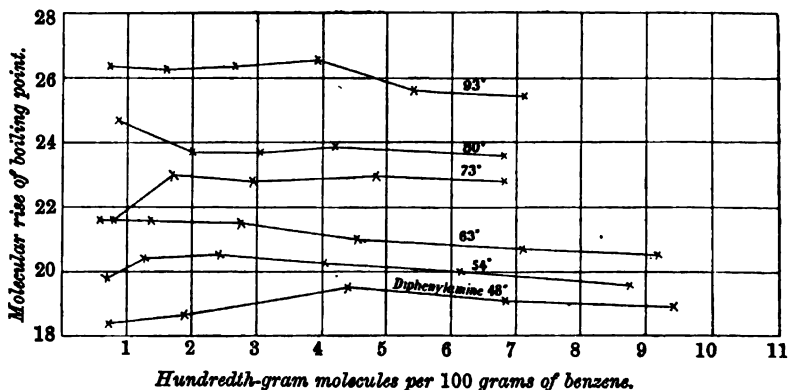
FIG. 2.—Phenanthrene.



values for  $\tau$  change but little. These values were used for calculating the mean molecular rise, and the first determination was not included in the mean if the rise of boiling point was less than 0.1.

The agreement in the double series carried out with phenanthrene and benzophenone is most satisfactory. The mean values for  $\tau$  never

FIG. 3.—Benzophenone.



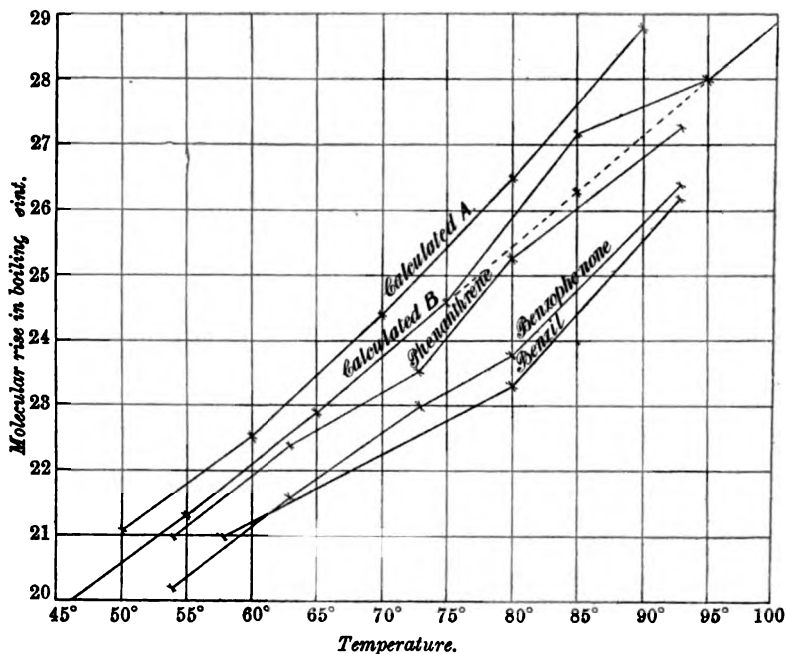
differ by more than 0.3, and for solutions of similar concentration the agreement for single determinations is, in many cases, within 0.1.

The regularity of the results obtained at different temperatures is well shown by the curves got by plotting  $\tau$  against the concentration

expressed in 1/100 gram-molecules of substance per 100 grams of solvent (Figs. 2 and 3). The curves are practically parallel; those for phenanthrene show a slight but distinct downward tendency, whilst the benzophenone curves are almost horizontal.

The variation of  $\tau$  with temperature is shown clearly by plotting the values of  $\tau$  for each substance at different temperatures against the temperature. This is done in Fig. 4. The curve for  $\tau$ , calculated

FIG. 4.



from the latent heat (calculated A) and from Ramsay and Young's determinations of the vapour pressures (calculated B), are also given. Below is a table of the data from which these were calculated :

TABLE II.

Temperature.	Heat of vaporisation in gram cal.	$RT^2/L$ .
50°	100.4	21.1
60	98.3	22.5
70	96.0	24.4
80	93.7	26.5
90	91.2	28.8

TABLE II (*continued*).

Temperature.	Pressure in cm.	$dp/dt$ .	Mean pressure.	$M$ .	$\frac{Mp}{dp/dt}$ .
40°	18.02	0.881	22.42	78	19.85
50	26.83	1.202	32.84	"	21.31
60	38.85	1.596	46.83	"	22.89
70	54.82	2.068	65.16	"	24.58
80	75.50	2.530	88.1	"	27.17
90	100.8	3.27	117.1	"	27.96
100	133.5	4.04	158.7	"	29.68
110	178.9				

*Mean Values of the Molecular Rise of Boiling Point at Different Temperatures.*

	54°.	58°.	63°.	73°.	80°.	93°.
Calculated A .....	21.6	22.2	23.0	25.0	26.5	29.5
Calculated B .....	21.05	21.6	22.4	24.25	25.5	27.8
Phenanthrene .....	21.0	—	22.4	23.55	25.25	27.3
Benzophenone .....	20.17	—	21.6	22.95	23.8	26.4
Benzil .....	—	21.0	—	—	23.3	26.2
General mean for phenanthrene and benzophenone ...	20.6	—	22.0	23.25	24.1	26.9

The molecular rise of boiling point, calculated from the variation of vapour pressure with temperature, forms, when plotted against the temperature, a very regular curve from  $-5^{\circ}$  to  $+145^{\circ}$ , the values increasing somewhat more rapidly than the temperature. The only value which does not lie well on the curve is that at  $85^{\circ}$ . This deviation is accounted for by the fact that the vapour pressures below and above  $80^{\circ}$  were determined in two separate researches (by Ramsay and Young, and Young respectively). In Young's paper, the vapour pressures calculated by means of Biot's formula and constants calculated from his own measurements are given. The calculated vapour pressure at  $80^{\circ}$  is smaller than that found by direct experiment, and is larger at  $90^{\circ}$ ; although the differences are small,  $dp/dt$  is decreased considerably. If  $\tau$  be calculated from the pressures given by Biot's formula for  $80^{\circ}$  and  $90^{\circ}$ , the value obtained falls well on the curve. This is shown by the dotted portion of the curve.

The molecular rise found at the various temperatures using phenanthrene as dissolved substance, agree closely with those calculated from the vapour pressure, the greatest difference being a little more than 2 well sat. The molecular rise with benzophenone is considerably smaller

than with phenanthrene. If smoothed curves be drawn, it will be seen that the difference is nearly the same at the different temperatures and amounts to about 0.8. It is well known that different values are obtained for the molecular rise at atmospheric pressure according to the substance dissolved, even though the substances cannot be considered as abnormal in the ordinary sense. That this difference is not due to association in the case of benzophenone is shown by the fact that the molecular rise does not decrease with concentration. It is interesting that the two closely related substances, benzophenone and benzil, give curves which agree closely with one another.

The molecular rise calculated from the heat of vaporisation is greater than that calculated from the variation of vapour pressure with temperature. The molecular rise found by direct experiment agrees much better with that calculated in the latter manner: a result which was hardly to be expected.

*Abnormal Substances.*

Columns 1 to 8 have the same meaning as in Table I (p. 688), column 9 gives the molecular weight found. The molecular weights are calculated with the mean molecular rise for phenanthrene and benzophenone:

TABLE III.

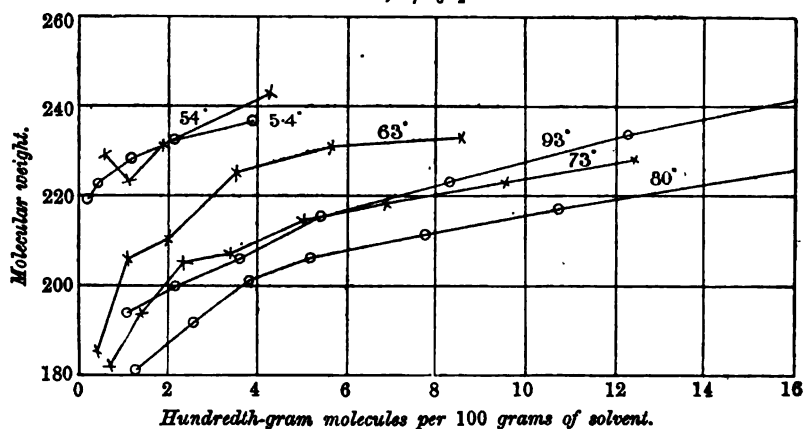
1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>Benzoic Acid, C<sub>7</sub>H<sub>6</sub>O<sub>2</sub> = 122.</i>								
22	31.0	53.7	24.21	0.1516	0.059	0.637	0.522	229
				0.3373	0.135	1.42	1.16	223
				0.5636	0.213	2.37	1.94	236
				1.2550	0.460	5.27	4.32	243
				1.616	0.585	6.78	5.56	248
				2.262	0.825	9.50	7.78	245
				3.001	1.083	12.60	10.33	247
23	48.3	63.1	22.19	0.1210	0.066	0.555	0.455	185
				0.2910	0.143	1.33	1.09	205
				0.5294	0.254	2.43	1.99	210
				0.926	0.416	4.25	3.48	225
				1.501	0.655	8.89	5.65	231
				2.2724	0.984	10.42	8.54	233
24	61.3	73.2	22.19	0.1806	0.106	0.829	0.679	182
				0.3680	0.202	1.69	1.38	194
				0.6402	0.333	2.94	2.41	205
				0.905	0.465	4.15	3.40	207
				1.324	0.660	6.07	4.98	214
				1.813	0.889	8.32	6.82	218
				2.527	1.208	11.60	9.50	223
				3.285	1.538	15.1	12.36	228

TABLE III. (continued).

1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>Benzoic Acid</i> , $C_7H_6O_2 = 122$ (continued).								
25	75.6	80.1	22.19	0.8430 0.7016 1.026 1.391 2.052 2.836 4.287 5.924	0.209 0.403 0.563 0.743 1.070 1.441 2.088 2.823	1.57 3.22 4.71 6.88 9.42 13.0 19.7 27.2	1.29 2.64 3.86 5.23 7.72 10.7 16.1 22.3	181 192 201 206 211 217 226 231
26	109.0	93.1	22.19	0.2894 0.5898 0.948 1.426 2.196 3.252 4.947	0.181 0.359 0.560 0.809 1.199 1.706 2.486	1.33 2.71 4.35 6.54 10.08 14.9 22.7	1.09 2.22 3.57 5.36 8.26 12.24 18.61	194 200 206 215 223 232 247

*Benzoic Acid.*

The results obtained are graphically expressed in Fig. 5. The temperature at which each series was carried out is shown. The curve for

FIG. 5.—*Benzoic acid*,  $C_7H_6O_2$ . Mol. wt. = 122.

benzoic acid in benzene (Beckmann, *Zeit. physikal. Chem.*, 1888, 2, 729) is also given. The freezing point of benzene is  $5.4^{\circ}$ . The values obtained by the boiling point method at  $54^{\circ}$  agree closely with those by the freezing point method. The curve at  $63^{\circ}$  lies much lower than

that at 54°, the difference being greatest in dilute solution, the difference between the curves decreases up to 80°. The 93° curve lies higher than that for 80°. The agreement in the molecular weights at 54° and 54° does not necessarily show that there is no change of association between these temperatures. It is well known that benzoic acid volatilises considerably at temperatures below 100°, and it boils at 134° under 12 mm. pressure. If the benzoic acid had a vapour pressure of between 3 and 4 mm. in a solution containing 6/100 gram-molecule per 100 grams benzene, this would raise the apparent molecular weight about 10 per cent., that is, more than 20 units. The apparent decreasing effect of change of temperature on the association as the temperature rises may be due to increase of vapour pressure of the benzoic acid with temperature, and the fact that higher values were obtained at 93° than at 80° might be due to the same cause.

Although the unknown influence of the vapour pressure detracts considerably from the value of the results with benzoic acid, it may safely be said that increase of temperature brings about a decrease of association between 54° and 80°, since the change of vapour pressure of the benzoic acid would tend to bring the molecular weights at different temperatures nearer together :

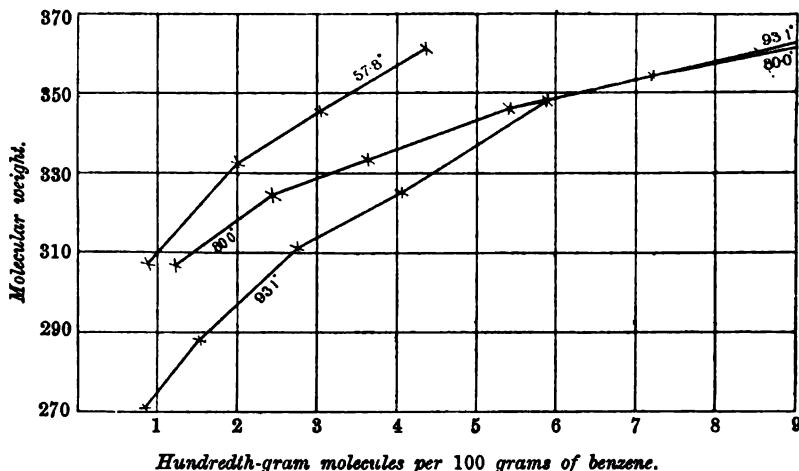
TABLE IV.

1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>o</i> -Bromobenzoic Acid, $C_7H_5O_2Br = 201$ .								
22	35.8	57.8	22.19	0.8872 0.885 1.341 1.914	0.124 0.262 0.382 0.521	1.78 4.08 6.15 8.78	0.884 2.02 3.06 4.37	307 332 345 361*
23	75.35	80.0	22.19	0.5388 1.074 1.599 2.382 3.176 4.225	0.193 0.364 0.529 0.758 0.989 1.278	2.47 4.93 7.34 10.7 14.6 19.4	1.23 2.45 3.65 5.44 7.25 9.64	307 325 333 346 354 364
24	109.0	93.1	22.19	0.3732 0.682 1.216 1.786 2.600 3.748 5.056 6.775	0.167 0.288 0.475 0.668 0.910 1.268 1.650 2.158	1.71 3.13 5.58 8.20 11.93 17.2 23.2 31.1	0.851 1.56 2.78 4.08 5.93 8.56 11.54 15.5	271 288 311 325 348 360 373 382

\* The substance apparently dissolved completely, but further addition of substance caused no increase of boiling point.

*o*-Bromobenzoic Acid.

Three series of determinations were made with this substance at 58°, 80°, and 93° respectively. The *o*-bromobenzoic acid was not sufficiently soluble to make a series of determinations at the freezing point. From the curves (Fig. 6), it will be seen that the molecular

FIG. 6.—*o*-Bromobenzoic acid,  $C_7H_5O_2Br$ . Mol. wt. = 201.

weight at 80° is, for similar concentrations, considerably smaller than at 58°, and the difference increases with the concentration. In dilute solutions, the 93° curve lies considerably below that for 80°, with increasing concentration, the curves approach one another and finally become practically parallel:

TABLE V.

1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>β</i> -Benzilmonoxime, $C_{14}H_{11}O_2N = 225$ .								
25	35.8	57.8	21.96	0.3852	0.185	1.79	0.794	231
				0.750	0.320	3.48	1.55	259
				1.115	0.441	5.17	2.30	280
				1.575	0.591	7.31	3.24	295
				2.033	0.716	9.43	4.19	314
				2.643	0.880	12.26	5.45	332

TABLE V. (continued).

1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>β</i> -Benzilmonoxime, $C_{14}H_{11}O_2N = 225$ (continued).								
26	75.5	80.0	22.19	0.1680 0.339 0.520 0.897 1.427 2.019	0.072 0.151 0.233 0.389 0.593 0.812	0.762 1.56 2.39 4.12 6.55 9.26	0.339 0.692 1.06 1.83 2.91 4.12	249 243 242 350 261 269
27	109.0	93.1	22.19	0.3670 0.718 1.034 1.610 2.097 2.700	0.180 0.350 0.488 0.723 0.896 1.097	1.68 3.30 4.74 7.39 9.54 12.39	0.748 1.46 2.11 3.28 4.24 5.51	249 251 259 273 284 301

*β*-Benzilmonoxime.

Determinations were carried out at 58°, 80°, and 93°. In the table of curves, the molecular weights found by the freezing point method in benzene (Auwers, *Zeit. physikal. Chem.*, 1893, 12, 701) and in naphthalene (Innes, *Inaug. Diss. Heidelberg*, 1896) are also given. Determinations with more concentrated solutions in benzene could not be carried out at the freezing point, because of the small solubility of the substance. *β*-Benzilmonoxime crystallises with benzene of crystallisation, the formula of the compound is  $2C_{14}H_{11}O_2N, C_6H_6$ . The abnormality in benzene might be considered to be due to the formation, in part, of this compound. It is impossible to decide in the present state of our knowledge whether this is really the case; it seems more probable, however, that the combination with the solvent does not affect the molecular weight to an appreciable extent in this instance.

From the curves (Fig. 7, p. 703), it will be seen that the association of *β*-benzilmonoxime decreases considerably with rise of temperature up to 80°, the association then seems to increase, the 93° curve lying somewhat higher than that for 80°; the greatest difference is about 4 per cent. :



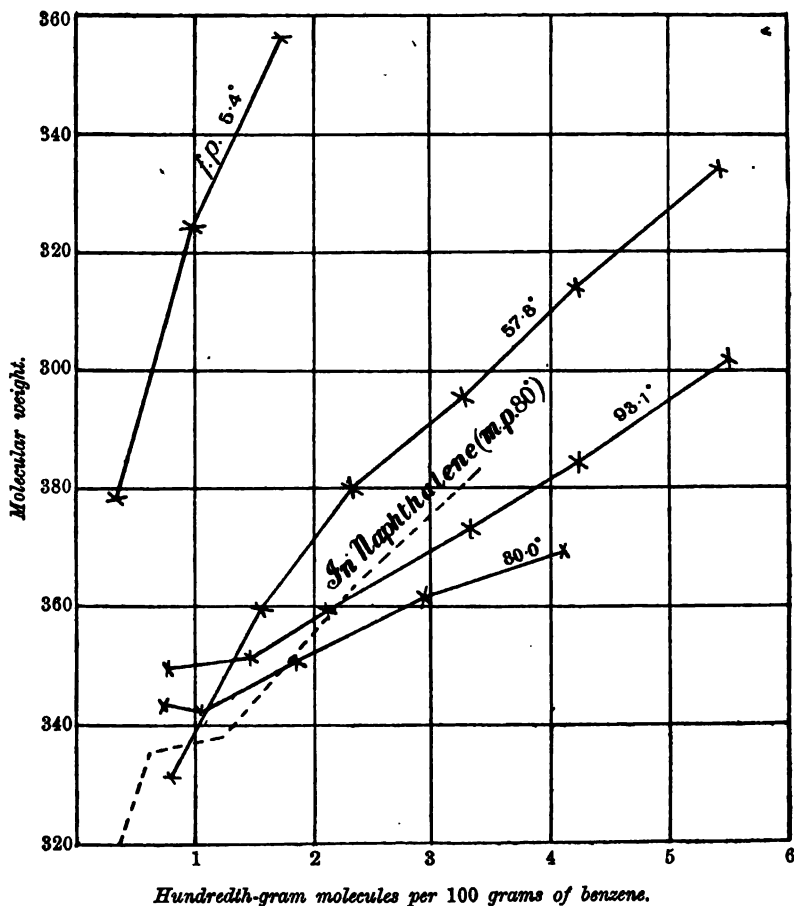
TABLE VI.

1.	2.	3.	4.	5.	6.	7.	8.	9.
<i>Dimethyl Tartrate, C<sub>6</sub>H<sub>10</sub>O<sub>6</sub> = 178.</i>								
28	31.0	53.7	24.74	0.3196 0.8606 1.470 2.057 2.898 4.000	0.147 0.337 0.520 0.662 0.821 1.000	1.31 3.53 6.04 8.45 11.91 16.43	0.74 1.99 3.39 4.75 6.69 9.23	186 218 242 266 302 342
29	43.3	63.1	22.19	0.1704 0.4402 0.816 1.355 2.086 2.917 3.932 5.122	0.083 0.214 0.367 0.556 0.764 0.957 1.156 1.344	0.984 2.02 3.74 6.22 9.57 13.39 18.04 23.51	0.553 1.13 2.10 3.49 5.38 7.52 10.14 13.20	207 208 225 246 276 307 343 385
30	61.28	73.2	22.19	0.2966 0.6744 1.207 1.836 2.894 4.134 5.213 6.233	0.162 0.339 0.567 0.794 1.091 1.371 1.671 1.751	1.36 3.09 5.54 7.51 11.84 16.90 21.31 25.69	0.962 1.74 3.11 4.22 6.65 9.50 11.98 14.44	195 212 227 247 283 322 354 383
31	73.5	79.2	22.19	0.2670 0.5528 0.990 1.662 2.528 3.919 5.025	0.159 0.301 0.500 0.751 1.029 1.371 1.592	1.23 2.54 4.54 7.63 11.60 18.0 23.1	0.69 1.42 2.55 4.38 6.51 11.2 14.35	185 202 218 244 271 315 348
32	109.0	98.1	22.19	0.4280 0.8590 1.459 2.002 3.103 4.170	0.266 0.492 0.780 0.997 1.351 1.613	1.96 3.94 6.69 9.18 14.24 19.14	1.10 2.215 3.76 5.16 8.00 10.75	198 215 230 247 282 318

*Dimethyl Tartrate.*

With increasing dilution the molecular weight of dimethyl tartrate tends towards the same value at the various temperatures, the molecular weight found being in every case near the normal (Fig. 8, p. 705). In more concentrated solution the molecular weight decreases with rise of temperature between 54° and 79°, the decrease increasing with the

temperature. The molecular weight at  $93^{\circ}$  is lower than that at  $79^{\circ}$  in solutions of moderate concentration, but the curves cross at a concentration of  $8.7/100$  mols. The curves are all slightly concave downwards, with the exception of that at  $93^{\circ}$ , which is almost straight.

FIG. 7.— $\beta$ -Benzilmonoxime.

The degree of concavity increases with the temperature up to  $79^{\circ}$ . An attempt was made to carry out a series of determinations of the molecular weight by the freezing point method. Only one determination could be made; at higher concentrations the substance sometimes separated out:

*Freezing Point Method.*

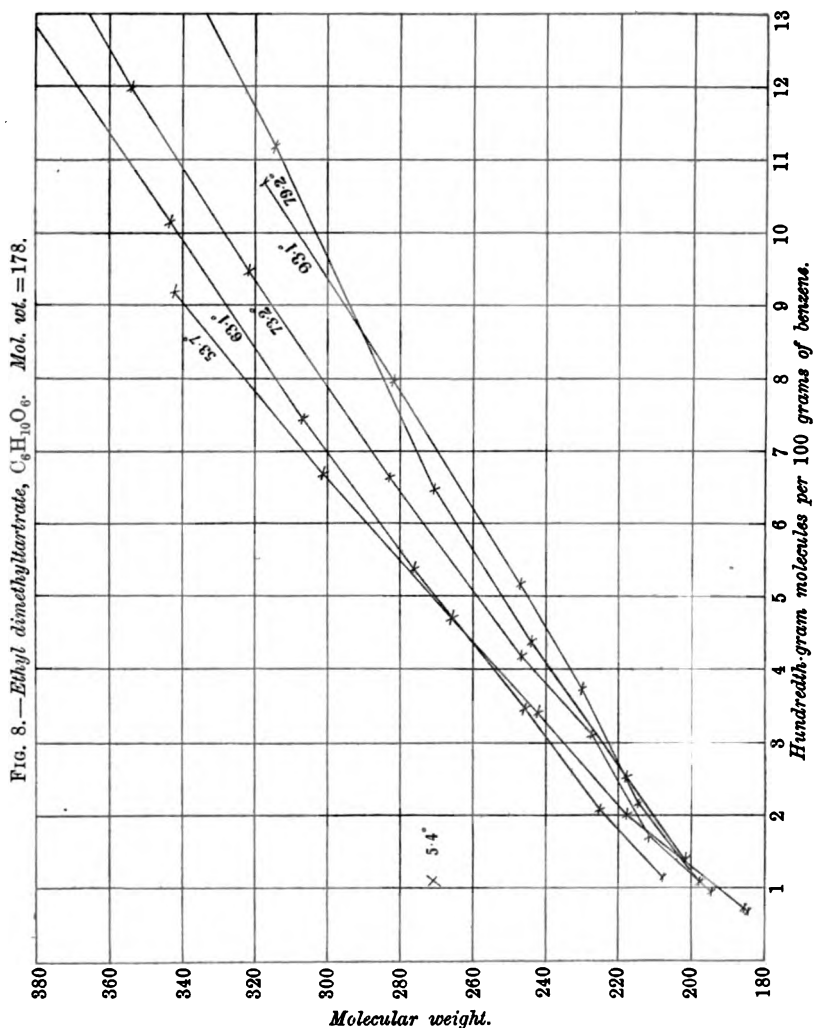
Weight of benzene.	Weight of substance.	Lowering of f. p.	Substance per 100 grams solvent.	Mols./100 per 100 grams solvent.	Mol. weight.
10.0	0.197	0.189	1.97	1.11	271

The association of all the substances examined decreased with rise of temperature up to 80°.

Thermodynamical reasoning shows that association may either increase or decrease with temperature, according as the heat of dissociation is negative or positive. Further, the heat of dissociation may change its sign with increase of temperature; if this change is from positive to negative, the dissociation increases up to the temperature at which the heat of dissociation is zero, then decreases. Instances of such a change have been observed for ionic dissociation by Arrhenius, and it is probable that among gaseous substances carbon dioxide,  $\text{CO}_2$ , silicon hydride,  $\text{SiH}_4$ , and selenium hydride,  $\text{SeH}_2$ , behave thus at high temperatures. The observed molecular weight of benzoic acid and of  $\beta$ -benzilmonoxime is greater at 93° than at 80° for all concentrations; that of *o*-bromobenzoic acid and of dimethyl tartrate is smaller in dilute solutions, in more concentrated solutions, the molecular weight of the former is the same at both temperatures, whilst that of the latter is greater at the higher temperature. This apparent decrease of dissociation with rise of temperature may possibly be due to a change of sign in the heat of dissociation. It does not, however, seem probable that this is the true explanation. If a change of sign actually occurred, we should expect this to take place at a different temperature for each substance. Further, increase of temperature brings about an increasing amount of dissociation of dimethyl tartrate up to 80°; that a further increase of 14° in the temperature should cause a decrease of dissociation is extremely improbable. The fact that the experiments at 93° were carried out at increased pressure, whilst those at the other temperatures were at reduced or atmospheric pressure, suggests that the high molecular weights at this temperature may be due to an error in the method. The constancy of the value of the molecular rise of boiling point at different concentrations for each of the three substances examined, as well as the position of the molecular rise of boiling point at this temperature on the temperature curve (Fig. 4), seems to show that the method is as accurate at increased as it is at reduced or atmospheric pressure. It does not seem probable that the increase of molecular weight at 93° is due to the influence of the solvent.

The heats of dissociation ( $Q$ ) of  $\beta$ -benzilmonoxime, benzoic acid, and *o*-bromobenzoic acid from double to single molecules were calculated by means of the equation :

$$\log_e \frac{x_2^2}{(1-x_2)V_2} - \log_e \frac{x_1^2}{(1-x_1)V_1} = \frac{Q}{2} \left( \frac{1}{T_1} - \frac{1}{T_2} \right),$$



in which  $x_1$  is the degree of dissociation at the absolute temperature  $T_1$   
 "  $x_2$  " " " " " $T_2$   
 "  $V_1$  is the volume occupied by one gram-molecule of the substance calculated as double molecules, at the temperature  $T_1$

in which  $V_2$  is the volume occupied by one gram-molecule of the substance calculated as double molecules, at the temperature  $T_2$ ,

„  $V$  was taken as the volume of benzene in litres in which one gram-molecule of the substance, calculated as double molecules, was dissolved, and  $V_1$  as equal to  $V_2$ .

„  $x$  was calculated by a slight modification of the equation used to calculate the degree of dissociation of a gas from its density.  $x = \frac{M-m}{m}$ .  $M$  is the molecular weight of the double molecule,  $m$  the molecular weight found.

The following data were used :

	Mols. 100	$m_1$ .	$m_2$ .	$x_1$ .	$x_2$ .	$T_1$ .	$T_2$ .	$V$ .	$Q$ .
$\beta$ -Benzilmon-oxime .....	1.73	356	264	0.258	0.704	278	331	13	14600
„ .....	„	264	249	0.704	0.807	331	353	14	19900
<i>o</i> -Bromobenzoic acid .....	3.00	344	328	0.169	0.232	331	353	8.18	7500
„ .....	2.00	332	318	0.211	0.264	331	353	12.3	5300
Benzoic acid .....	3.00	220	195	0.117	0.251	336	353	8.18	23000

The heat of dissociation of gaseous  $N_2O_4$  ( $t_1 = 26.7^\circ$ ,  $t_2 = 111.3^\circ$ ) is 12,900 calories; that of iodine vapour, 28,500 cal.; acetic acid, 20,000 cal., and dimethyl ether hydrochloride, 8600 cal. It thus appears that the heat of dissociation of a substance in solution is of the same order as that usual for a vapour. The above result adds another instance to the many already known of the close analogy between the behaviour of a substance in solution and in the state of vapour.

The above experiments were carried out in the Chemical Laboratories of the University of Birmingham. I should like to take this opportunity of thanking Professor Percy Frankland for his kindness in supplying most of the apparatus required for the experiments.

UNIVERSITY COLLEGE,  
LIVERPOOL.

LXXIII.—*The Preparation of Absolute Alcohol from Strong Spirit.*

By SYDNEY YOUNG, D.Sc., F.R.S.

OWING to the fact that ethyl alcohol, like *n*-propyl, isopropyl, and *tert*-butyl alcohols, although miscible with water in all proportions, forms with it a mixture of constant boiling point which distils without change of composition at a temperature lower than either component, it is impossible by any process of fractional distillation to separate the pure alcohol from a dilute solution. All that can be done is to separate the mixture of constant boiling point on the one hand, and water on the other, from the solution. In the case of the other alcohols referred to, if we remove a portion of the water from the mixture of constant boiling point by some other method, then by fractional distillation of the stronger alcohol with a very efficient still-head we can effect its separation into the pure alcohol and the mixture of constant boiling point.

Pure ethyl alcohol, however, boils less than  $0.2^{\circ}$  higher than the mixture of minimum boiling point, and such a separation is therefore impracticable.

The method which has invariably been employed to prepare absolute alcohol is to treat the strongest spirit obtainable by distillation with a dehydrating agent, and the action of such agents has been studied by many investigators, notably by Mendeléeff and by Squibb.

In his classical paper on this subject, Mendeléeff (*Ann. Phys. Chem.*, 1869, [ii], 138, 230) discusses the behaviour of different dehydrating agents and concludes that freshly ignited lime is the only substance capable of giving good results, and that even when lime is employed special precautions must be taken.

The results obtained by Mendeléeff with four different specimens show excellent agreement, the greatest difference from the mean sp. gr. at  $0^{\circ}/4^{\circ}$ , 0.806254, being only 0.000011, but Mendeléeff himself states that when the alcohol was freshly distilled over lime he noticed an ethereal odour which, however, disappeared on repeated distillation, although the sp. gr. remained unchanged. The value 0.80625 has been almost universally adopted as the correct sp. gr. at  $0^{\circ}/4^{\circ}$ , but Squibb (*J. Amer. Chem. Soc.*, 1893, 15, 126) has obtained even lower values by slow percolation through lime. In an earlier investigation, Squibb had found the sp. gr. 0.79350 at  $15.6^{\circ}/15.6^{\circ}$ , which corresponds to 0.80581 at  $0^{\circ}/4^{\circ}$ , but in the paper referred to he states that after long contact with lime and subsequent percolation many times through an improved apparatus, alcohol was obtained with a somewhat higher

specific gravity. The results were not perfectly concordant, the mean of the best being given as  $0.793562$  at  $15.6^{\circ}/15.6^{\circ}$ , corresponding to  $0.80587$  at  $0^{\circ}/4^{\circ}$ . Squibb states that in his opinion absolute alcohol had not yet been obtained.

When two liquids of different chemical type are distilled together, a definite mixture of minimum boiling point in many cases distils over first, the last portion of the distillate consisting of that component which was originally present in excess. Ethyl alcohol may be regarded as a derivative of water and as belonging to the water type  $H \cdot O \cdot C_2H_5$ , or as a derivative of ethane, or, more generally, of a paraffin,  $C_2H_5 \cdot OH$ . In its properties, it exhibits analogies in some respects to water and in others to the paraffins. Most dehydrating agents which react or combine with water behave in a somewhat similar manner towards the alcohols, though to a less degree, and to a diminishing extent as the molecular weight increases, and this accounts for the unsatisfactory results obtained with them. Thus phosphoric oxide gives phosphoric acid with water, and a mixture of ethyl hydrogen phosphates with ethyl alcohol; with barium oxide, water forms barium hydroxide, whilst ethyl alcohol forms, according to Forcrand, a compound  $3BaO, 4C_2H_5O$ ; sodium acts in precisely the same way on the alcohols as on water, but the intensity of the action diminishes rapidly as the complexity of the alkyl group increases; calcium chloride forms a crystalline hexahydrate with water, and a crystalline tetra-alcoholate with methyl or ethyl alcohol; the behaviour of anhydrous copper sulphate is striking; it dissolves rapidly in water, and, on evaporation, crystals of  $CuSO_4 \cdot 5H_2O$  are deposited; in methyl alcohol, it dissolves slowly, but to a considerable extent, giving a blue solution from which, according to Forcrand, greenish-blue crystals of  $CuSO_4 \cdot CH_4O$  may be obtained; anhydrous copper sulphate is, however, quite insoluble in ethyl alcohol, and will extract some water from strong spirit, but it is not a sufficiently powerful dehydrating agent to remove the whole.

If we compare the homologous normal primary alcohols together, we find that in other respects also, as the molecular weight rises, the alkyl group has increasing, and the hydroxyl group diminishing, influence, and that the properties recede from those of water and approach those of the corresponding paraffin. The table of boiling points on p. 709 shows this clearly.

Thus methyl alcohol boils only  $35.3^{\circ}$  lower than water, but  $228.7^{\circ}$  higher than methane, whilst cetyl alcohol boils  $244^{\circ}$  higher than water, but only  $56.5^{\circ}$  higher than the corresponding paraffin. Again, whilst methyl, ethyl, and propyl alcohols are miscible in all proportions with water, butyl alcohol is only partially miscible, and cetyl alcohol is practically non-miscible with water.

Lastly, while a mixture of methyl alcohol and water distils normally,

Number of carbon atoms.	Boiling points.				
	Paraffin.	Δ.	Alcohol.	Δ.	Water.
1	-164°	+228·7°	+64·7°	-35·3°	100°
2	-98	171·3	78·3	-21·7	—
3	-45	142·4	97·4	-2·6	—
4	+1	116·0	117·0	+17·0	—
5	36·3	101·7	138·0	38·0	—
6	69·0	88·0	157·0	57·0	—
7	98·4	77·6	176·0	76·0	—
8	125·6	70·4	196·0	96·0	—
16	287·5	56·5	344·0	244·0	—

both components being easily separated, ethyl and propyl alcohols form, with water, mixtures of minimum boiling point, and the behaviour of butyl alcohol and water approaches that of two non-miscible liquids.

We cannot well study the miscibility of the alcohols with the corresponding paraffins, because the first four are gaseous at the ordinary temperature and most of them are difficult to prepare in a pure state. Normal hexane, however, can be obtained without much difficulty, and we find that, although the lowest alcohols are miscible with this hydrocarbon in all proportions, they form with it mixtures of minimum boiling point. Benzene is much more easily obtained than hexane, and behaves in a similar manner. The behaviour of mixtures of benzene with the lower alcohols has been studied by Miss Fortey and myself, and is fully considered in a separate paper; it will be sufficient here to state that whilst methyl, ethyl, *isopropyl*, *n*-propyl, *tert*.butyl, and *isobutyl* alcohols form mixtures of minimum boiling point with benzene, *isoamyl* alcohol does not.

Thus ethyl alcohol forms mixtures of minimum boiling point, both with water and with benzene (or hexane), whilst benzene and water are practically non-miscible and distil over together at a temperature lower than the boiling point of either pure liquid; it seemed reasonable to expect that a particular mixture of all three liquids would boil constantly at a still lower temperature. The original mixture would, in that case, tend to separate on distillation into three instead of two fractions:—(1) a definite mixture of all three liquids boiling at a lower temperature than any of the three components, or than any mixture of any two of them; (2) a mixture of two components boiling at a lower temperature than any single one; (3) that component which was originally in excess.

When aqueous alcohol is distilled with a dehydrating agent, the water is more or less completely retained in the still, the dried alcohol passing over as the distillate; if, however, a mixture of ethyl alcohol,



benzene, and water behave as suggested above, it should be possible to reverse the process, the water being carried over in the first part of the distillate and pure alcohol coming over last. Such a method would be advantageous for this reason, among others, that it is almost always easier to separate the least volatile component of a mixture in a pure state by distillation than the more volatile components. These anticipations were fulfilled, and it was, in fact, found possible to eliminate the water from strong spirit by distillation with benzene.

In all the experiments carried out in connection with this investigation, I have had the advantage of the able co-operation of Miss E. O. Fortey, B.Sc.

The following table gives the boiling points of ethyl alcohol, benzene, and water, and of the mixtures of constant boiling point that they can form, also the composition of these mixtures.

The benzene-water values were calculated from the known vapour pressures of benzene and water, these two liquids being practically non-miscible, and their correctness was confirmed by actual experiments; the other values were determined experimentally:

Liquid of constant boiling point.	Boiling point.	Percentage composition.		
		Alcohol.	Water.	Benzene.
1. Alcohol, water, and benzene (W.A.B.)...	64·85°	18·5	7·4	74·1
2. Alcohol and benzene ... (A.B.)...	68·25	32·41	—	67·59
3. Water and benzene ..... (W.B.)	69·25	—	8·83	91·17
4. Alcohol and water ..... (A.W.)...	78·15	95·57	4·43	—
5. Alcohol ..... (A.)...	78·3	100	—	—
6. Benzene ..... (B.)...	80·2	—	—	100
7. Water ..... (W.)	100·0	—	100	—

It will be seen that the lowest boiling point is that of the ternary mixture (W.A.B.), so that whatever mixture of the three liquids is distilled—unless one constituent is present in relatively very small quantity—this ternary mixture will come over first. If there is more than sufficient benzene to carry over the whole of the water, and if the alcohol is present in excess, the ternary mixture will be followed by the binary (A.B.) mixture, and the last substance to come over will be alcohol. This is the case, for instance, if we distil a mixture of equal weights of benzene and, say, 93 per cent. (by weight) alcohol with a very efficient still-head. The distillate is at first turbid, and on standing separates into two layers, although the original mixture is quite clear; the temperature remains constant at 64·85° for a long time, it then rises slowly, but with increasing rapidity, to the middle

temperature,  $66.55^{\circ}$ , between  $64.85^{\circ}$  and  $68.25^{\circ}$ , when the distillate ceases to be turbid; the temperature then rises more and more slowly, and becomes nearly steady for some time at or a little below  $68.25^{\circ}$ , when the binary (A.B.) mixture comes over. Then the temperature rises again with increasing rapidity, and very rapidly indeed as it passes the middle temperature,  $73.3^{\circ}$ , between  $68.25^{\circ}$  and  $78.3^{\circ}$ ; afterwards, the rise becomes slower and slower until the boiling point of alcohol is reached.

It should thus be theoretically possible to carry over the whole of the water in the first fraction and to remove the whole of the remaining benzene in the second, leaving pure alcohol in the last. It will, however, be noticed that the difference between the boiling points of the ternary (W.A.B.) mixture and the binary (A.B.) mixture is only  $3.4^{\circ}$ , so that the separation is a difficult one and in practice it was found that even when the mixture was distilled through an 18 column Young and Thomas dephlegmator at the rate of 1 drop per second, the alcohol in the final distillate, though containing the merest trace of benzene, still retained about 1.4 per cent. of water as compared with 7.4 per cent. in the original alcohol.

By redistilling the partially dehydrated alcohol once or twice with a further quantity of benzene, the water could, however, be finally eliminated.

It is convenient to collect the distillate in four fractions:—

I. From  $64.85^{\circ}$  to about  $67.5^{\circ}$ . This consists mainly of the ternary (W.A.B.) mixture.

II. From  $67.5^{\circ}$  to about  $73^{\circ}$ . This consists chiefly of the binary (A.B.) mixture.

III. From about  $73^{\circ}$  to  $78.3^{\circ}$ . The distillate should be collected in III for a little time after the temperature has become constant at  $78.3^{\circ}$  to remove the benzene as completely as possible. This fraction is much richer in alcohol than II; it should be relatively very small in amount.

IV. The dehydrated alcohol; it is not essential that this should be distilled, it may simply be run off from the still.

*Fraction I, boiling at  $64.85^{\circ}$  to about  $67.5^{\circ}$ .*

This distillate is turbid and separates into two layers, the smaller (and usually but not necessarily the lower) layer consisting of water, a good deal of alcohol, and some benzene, the larger layer consisting of benzene with a good deal of alcohol and a little water. On adding more water, shaking, and allowing to stand, two layers are again formed; the lower one, A, contains most of the alcohol and water with very little benzene; the upper one, B, contains nearly all the benzene

with very little alcohol and water. The two layers should now be separated and the benzene washed once or twice with water to remove the alcohol (and also the water, since alcoholic benzene dissolves more water than pure benzene) more completely; the water may be added to A.

The two liquids, A and B, should now be distilled, preferably with an efficient still-head.

*Distillation of A.*—On distillation, this liquid tends to separate into three fractions: (1) a very small quantity of the ternary (W.A.B.) mixture boiling at  $64.85^{\circ}$ ; (2) the binary (A.W.) mixture boiling at  $78.15^{\circ}$ ; (3) water. The whole of the benzene comes over below  $78.15^{\circ}$ , and this small fraction may be added to other quantities of the ternary mixture. The rest of the distillation consists simply in the recovery of strong spirit from dilute alcohol.

*Distillation of B.*—On distillation, B tends to separate into three fractions: (1) a minute quantity of the ternary mixture, but this may be absent if the benzene has been very thoroughly washed with water; (2) the binary (W.B.) or possibly (A.B.) mixture, also; exceedingly small in amount; (3) pure benzene.

There is no advantage in keeping the two first fractions separate, they may be collected together and added to the ternary mixture from other distillations. After the temperature has reached  $80.2^{\circ}$ , the liquid in the still consists of pure benzene and there is no necessity to distil it.

*Fraction II, boiling from about  $67.5^{\circ}$  to about  $73^{\circ}$ .*

This distillate is clear and consists chiefly of the binary (A.B.) mixture, but it contains a little water. Dilute alcohol and benzene might be obtained from it by addition of water, but it is more advantageous to add it to the next mixture of strong spirit and benzene that is to be distilled. If equal weights of strong spirit and benzene are again taken and the (A.B.) mixture is added, the alcohol obtained will be drier and the quantity a little larger. The fractions obtained in this case will be the same as before, but fraction II (b. p.  $67.5-73^{\circ}$ ) will be larger. If at any time the quantity becomes too large to be made use of in this way, water may be added to a portion and pure benzene and strong spirit recovered as described under I.

*Fraction III, boiling at about  $73^{\circ}$  to  $78.3^{\circ}$ .*

This fraction should be relatively small; it consists chiefly of alcohol with some benzene and very little water. It is not worth while to redistil the fraction from a single operation, but the fractions from a series of distillations should be added together and stored until the quantity is large enough to be redistilled.

On distillation, fraction (1) will be absent or very small ; fraction (2) will be fairly large ; fraction (3) about the usual small quantity ; fraction (4) large. Thus an additional quantity of partially dehydrated alcohol will be obtained.

*Fraction IV, boiling at 78.3°.*

This fraction consists of alcohol containing no more than a trace of benzene and nearly free from water. It is impossible to state definitely what percentage of water will remain in the alcohol ; the more efficient the still-head, the slower the distillation and the larger the amount of benzene originally added, the drier will the alcohol be.

In this process, the whole of the dehydrating agent, benzene, is recovered except the small amount lost by evaporation. There need also be hardly any loss of alcohol. As there is no chemical reaction, there is no possibility of introducing any impurity into the alcohol except, perhaps, a minute trace of benzene.

A considerable number of distillations with an 18 column Young and Thomas dephlegmator were carried out by this method at the rate of 1 drop per second. The alcohol employed was obtained from Kahlbaum ; its sp. gr. at 0°/4° was 0.82907, and it therefore contained 7.4 per cent. of water by weight ; it was quite free from other impurities.

After the temperature had reached 78.3°, the residual alcohol was collected in fractions and the sp. gr. of the first and last were, as a rule, determined. The results obtained were as follows :

(i) A mixture of 325 grams of 92.6 per cent. alcohol (sp. gr. 0.82907) and 325 grams of benzene (dried with sodium) was distilled. After the temperature had reached 78.3°, the following fractions were collected :

	Weight.	Sp. gr. at 0°/4°.	Percentage of water by weight from Mendeleeff's data.
1.....	20.9 grams.	0.81176	1.85
2.....	85.6 „	—	—
3.....	35.7 „	0.80976	1.10
Residue ...	22.8 „	—	—
	<hr/> 165.0 „		

It is very probable that the first fraction was in this case collected a little too soon, and contained a perceptible amount of benzene, which would raise its sp. gr.

(ii) Similar to the first, but the benzene was added in three portions. The weight of each liquid was 200 grams, and that of the dehydrated alcohol 89.5 grams. The sp. gr. of the first and last fractions

were 0.81043 and 0.80946, corresponding to 1.40 and 1.03 per cent. of water respectively.

(iii) A mixture of 254 grams of alcohol of sp. gr. 0.81033 (water 1.37 per cent.) was distilled with 169 grams of benzene. At 78.3°, the results were as follows :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1.....	27.8 grams.	0.80741	0.38
2.....	48.3 „	—	—
3.....	56.6 „	0.80683	0.13
Residue ...	11.5 „	—	—
	<hr/> 144.2 „		

(iv) The mixture distilled consisted of 282 grams of 92.6 per cent. alcohol, 282 grams of benzene, and 270 grams of binary (A.B.) mixture from previous distillations :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1.....	23.6 grams.	—	—
2.....	33.6 „	0.80822	0.62
Residue ...	108.7 „	—	—
	<hr/> 165.9 „		

(v) To 275 grams of 92.6 per cent. alcohol and 275 grams of benzene, 379 grams of a previous distillate collected between 66.5° and 78.3° was added :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1.....	18.6 grams.	—	—
2.....	23.7 „	0.80789	0.50
Residue ...	121.3 „	—	—
	<hr/> 163.6 „		

(vi) The 92.6 per cent. alcohol was first redistilled to remove a little water. A mixture of 275 grams of redistilled alcohol, 275 grams of benzene, and 254 grams of the fraction collected from the previous distillation between 67.35° and 78.3° was distilled :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1.....	17.3 grams.	—	—
2.....	22.0 „	0.80761	0.47
Residue ...	132.0 „	—	—
	<hr/> 171.3 „		

(vii) The mixture distilled consisted of 289 grams of alcohol, con-

taining a little more than 0·3 per cent. of water and 192 grams of benzene :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1.....	12·4 grams.	—	—
2.....	24·2 „	0·80660	about 0·1
3.....	67·1 „	—	—
4.....	53·0 „	0·80638	trace
Residue ...	15·0 „	—	—
	<hr/>		
	171·7 „		

(viii) A mixture consisting of 99·6 per cent. alcohol, (A.B.) fractions from previous distillations, and benzene, the whole estimated to contain 370 grams of alcohol and 310 grams of benzene, was distilled :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1.....	20·8 grams.	—	—
2.....	22·9 „	0·80673	about 0·11
3.....	94·4 „	—	—
4.....	24·9 „	0·80634	dry
Residue ...	39·0 „	—	—
	<hr/>		
	202·0		

(ix) The whole of the driest alcohol, 371·5 grams, was distilled with 249 grams of benzene :

	Weight.	Sp. gr. at 0°/4°.
1.....	26·4 grams.	0·80645
2.....	102·3 „	—
3.....	29·5 „	0·80636
Residue .....	25·3 „	—
	<hr/>	
	183·5	

(x) The alcohol from the last distillation, 182·3 grams, was distilled with 90 grams of benzene :

	Weight.	Sp. gr. at 0°/4°.
1.....	24·6 grams.	0·80644
2.....	20·4 „	—
3.....	36·0 „	0·80634
Residue .....	14·0 „	—
	<hr/>	
	95·0 „	

In the earlier distillations, the sp. gr. of the first portions of alcohol that came over at 78·3° was distinctly higher than that of the later portions ; weaker alcohol was, in fact, being partially separated from stronger alcohol. In later distillations, when the dehydration was

more complete, this difference of sp. gr. was considerably less, and in the last two it was very small, although still noticeable.

The sp. gr. of the last and best fraction was nearly the same in the last four distillations, 0.80638, 0.80634, 0.80636, 0.80634; mean, 0.80635.

The only effect of the eighth distillation was to reduce the difference between the sp. gr. of the first and last fractions of alcohol, and the redistillation of this alcohol with more benzene produced no further change. It seemed probable, therefore, that the whole of the water was removed, and that the slight difference in sp. gr. between the first and last fractions might be due to a very small amount of residual benzene, which, like water, would raise the sp. gr.

As already stated, *n*-hexane forms mixtures of constant boiling point with alcohol and with alcohol and water, and may be used for dehydrating alcohol. It possesses the advantage that the hexane-alcohol mixture can be separated very readily by distillation from the dehydrated alcohol. Again, when hexane and benzene are distilled together, the hexane will carry down more than 10 per cent. of benzene without any rise of temperature, a mixture of minimum boiling point—a few hundredths of a degree below that of hexane—containing about 5 per cent. of benzene, being probably formed.

It seemed possible, then, that if alcohol dehydrated with benzene were distilled with hexane, any minute residual quantity of benzene would be carried down in the hexane-alcohol fraction, and that the hexane itself could be completely eliminated. If, however, any hexane remained, the first fraction should have a lower sp. gr. than the last, since hexane is much lighter than alcohol.

A fresh quantity of alcohol was dehydrated with benzene, and 127.7 grams of this alcohol (sp. gr. 0.80638 at 0°/4°) were distilled with 128.4 grams of *n*-hexane freshly distilled over phosphoric oxide. The temperature remained quite constant at 58.65° for a long time, and when it changed, the rise to 78.3° was exceedingly rapid. The alcohol was, as usual, collected in fractions, with the following results:

	Weight.	Sp. gr. at 0°/4°.
1.....	22.3 grams.	0.80629
2.....	13.7 „	—
3.....	30.0 „	0.80627
Residue .....	8.8 „	—
	<hr/> 74.8 „	

The difference between the two sp. gr. was now practically within the limits of experimental error, although the tendency seemed to be still in the same direction. The value 0.80627 may, I think, be taken

as very close indeed to the true sp. gr. of ethyl alcohol at  $0^{\circ}/4^{\circ}$ . It agrees very well indeed with the sp. gr. observed by Mendeléeff, 0.806254, and the very low values observed by Squibb appear to be due to some chemical action of the lime on the alcohol, probably to the presence of a little ether.

My thanks are due to the Government Grant Committee of the Royal Society for a grant by means of which a great part of the expense of this investigation and of those described in this series of papers was defrayed.

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#### LXXIV.—*The Properties of Mixtures of the Lower Alcohols with Water.*

By SYDNEY YOUNG, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

METHYL and ethyl alcohols are commonly regarded as exceedingly hygroscopic substances from which the last traces of water can only be removed by means of the strongest dehydrating agents. Ethyl, *n*-propyl, isopropyl, and *tert.* butyl alcohols, which are miscible in all proportions with water, are known to form mixtures of constant boiling point with that substance, distilling at lower temperatures than the pure alcohols. In the last three cases, these mixtures, which have a definite composition when distilled under a given pressure, have been regarded as hydrates of the alcohols. The experiments of Konowaloff (*Ann. phys. Chem.*, 1881, [iii], 14, 34), however, on the vapour pressures of mixtures of the lower alcohols with water, seem to indicate that it should be possible to separate pure methyl alcohol from its aqueous solution by fractional distillation, and they throw great doubt on the existence of definite hydrates of the alcohols. Konowaloff found, in fact, that the vapour pressures of mixtures of methyl alcohol and water are always intermediate between those of the components, the curve showing the relation between vapour pressure and percentage composition at constant temperature lying fairly evenly between the extreme points. In the case of ethyl alcohol and water, there was far greater curvature, and the vapour pressure curve for mixtures of *n*-propyl alcohol with water was found to resemble that representing the behaviour of a partially miscible pair of liquids, such as isobutyl alcohol and water.

From this, it appears improbable that the formation of mixtures of constant boiling point can be due to increasing attraction between the molecules of the alcohols and those of water.



Further reasons against the assumption that a definite hydrate of *n*-propyl alcohol exists were brought forward in a paper read by one of us in conjunction with Dr. Ramsay (Proc., 1888, 4, 101), and, more recently, Thorpe (Trans., 1897, 71, 920) has shown the incorrectness of the usual statement that there are three definite hydrates of *iso*-propyl alcohol.

A more complete investigation of the nature and properties of mixtures of the alcohols with water than had yet been carried out seemed to be desirable, and the results of this investigation are described in the present paper.

### I. *Methyl Alcohol and Water.*

The older determinations of the boiling point and sp. gr. of methyl alcohol are very discordant and are invariably too high. This has been attributed to insufficient purification and especially to the presence of water, which, it is stated, can only be removed with great difficulty. All the more recent observers have used dehydrating agents such as lime, sodium, copper sulphate, or potassium carbonate.

The investigation of Dittmar and Fawsitt (*Trans. Roy. Soc. Edin.*, 1888, 33, 509) is generally regarded as the most complete, and their values of the sp. gr. of the alcohol and of mixtures of the alcohol with water are considered to be extremely accurate. The sp. gr. of the alcohol observed by Ramsay and Young (*Phil. Trans.*, 1887, 178, 313) agrees very well with that of Dittmar and Fawsitt. The boiling point, calculated from Biot's formula, was 64.9°, that of Dittmar and Fawsitt being 64.97°, but the boiling points actually observed by Ramsay and Young were somewhat lower, the final values being 64.7° and 64.75°.

In both cases, dehydrating agents were used, baryta, lime, and anhydrous copper sulphate by Dittmar and Fawsitt, sodium (repeatedly) by Ramsay and Young.

About 550 grams of Kahlbaum's purest methyl alcohol, free from acetone, were distilled through an 18 column Young and Thomas dephlegmator and the sp. gr. of the first fraction (92.4 grams) and of a later fraction (60 grams), collected after 405 grams had come over and when the temperature had risen 0.1°, were determined. The distillation was completed, the temperature at the last rising to 66.4°, and the residue in the still was then distilled from a small bulb, when the temperature rose from 69.3° to the boiling point of water.

The sp. gr. at 0°/4° of the first fraction was 0.81003, and of the later one 0.81017. Thus, although the original alcohol was proved to contain a little water, the sp. gr. of the first fraction was actually lower than that of any specimen hitherto obtained by the action of dehydrating agents. On redistilling the first fraction through the 18 column

dephlegmator, the sp. gr. of the distillate was very slightly lower, the value observed being 0·81000.

It appeared then that water could be completely removed by fractional distillation, but to confirm this conclusion it seemed advisable to fractionate a dilute alcohol. A mixture of 200 grams of pure alcohol with 40 grams of water was distilled through the same dephlegmator, and it was found that only a little water was carried over, for the sp. gr. of the first and of a later fraction were 0·81013 and 0·81025 respectively. Redistillation of the first fraction reduced its sp. gr. to 0·80998, the same value as before within the limits of experimental error.

The redistilled alcohol was then distilled over sodium, when it was found that both boiling point, 64·71°, and sp. gr. 0·81001 were unaltered.

The observed boiling points and sp. gr. of pure methyl alcohol are tabulated below.

The value of  $dp/dt$  at the boiling point is 29·6 mm. per degree.

Pressure.	Boiling points.		Sp. gr. at 0°/4°.
	Temperature observed.	Corr. to 760 mm.	
768·75 mm.	64·95°	64·65°	—
772·6    ,,	65·13	64·70	—
739·5    ,,	64·02	64·71	0·81003
749·5    ,,	64·42	64·77	0·81000
740·7    ,,	64·04	64·69	0·80998
738·75   ,,	63·99	64·71	0·81001
Mean 64·70		Mean 0·81000	

From these results, it is clear that, as was anticipated from Konovaloff's curves, fractional distillation with an efficient still-head, without the use of dehydrating agents, is sufficient to eliminate the last traces of water from dilute methyl alcohol and, indeed, it appears doubtful whether perfectly satisfactory results can be obtained by the use of dehydrating agents alone.

## II. Ethyl Alcohol and Water.

It was noticed by Mendeléeff (*Ann. Phys. Chem.*, 1869, [ii], 138, 230), and earlier by Sömmering, that when ethyl alcohol containing but little water, say about 2·5 per cent. by weight, is distilled, the first portions of the distillate contain rather more water than the later ones, but they apparently did not recognise the fact that the boiling point of the weaker alcohol is really slightly lower than that of pure alcohol. It is well known, from results obtained on the large scale, that by no

system of fractional distillation of weak spirit can alcohol of much more than 95 per cent. by weight be obtained.

Le Bel (*Compt. rend.*, 1879, 88, 912) observed that alcohol containing a little water has a slightly higher vapour pressure than pure alcohol.

Linebarger (*Chem. News*, 1894, 70, 52) determined accurately the boiling points of various mixtures of alcohol and water, his concentrations being expressed in parts of water in 100 of alcohol. He observed a minimum boiling point with about 4.5 parts of water, the actual temperature given for 4.497 parts of water being  $77.990^{\circ}$  under a pressure of 756 mm., that of alcohol, with 0.241 part of water, being  $78.091^{\circ}$ , and with 9.222 being  $78.088$ . This would give a difference of a little more than  $0.1^{\circ}$  between the boiling points of pure alcohol and of the mixture of constant boiling point.

Quite recently, Noyes and Warfel (*J. Amer. Chem. Soc.*, 1901, 23, 463) have determined the boiling point curve for aqueous alcohol, and find that 96 per cent. alcohol (97.45 per cent. by volume) has a minimum boiling point  $78.174^{\circ}$ , whilst that of absolute alcohol, and also of 90.7 per cent. alcohol, is  $78.30$ . This would give a difference of  $0.126^{\circ}$  between the two boiling points.

This difference is so small that it seemed hopeless to attempt a separation of either pure alcohol or the mixture of constant boiling point by fractional distillation of spirit containing more than about 96 per cent. of alcohol, but it was repeatedly observed that a partial separation could be effected. As the difference in boiling point between the mixture of constant boiling point and water is considerable, it seemed not impossible, especially as similar mixtures of water with other alcohols were very easily obtained, that fractional distillation of weak spirit would yield, not only pure water, but also the mixture of minimum boiling point without much difficulty.

The question, however, whether the two components of a mixture—either pure substances or mixtures of constant boiling point—can be easily separated by fractional distillation does not depend solely, or indeed chiefly, on the difference between the boiling points. The form of the curve representing the relation between the boiling points and molecular composition of various mixtures must be taken into account, and in this case the curve is exceedingly flat near the minimum boiling point. This fact, which is more fully discussed in the paper on fractional distillation as a method of quantitative analysis (this vol., p. 752), explains the difficulty actually experienced in separating the mixture of constant boiling point.

As a matter of fact, it was found on distilling a quantity of 92.6 per cent. alcohol that, although the strength rose rapidly at first, the improvement became slower and slower, and even after seven

distillations with the 18-column dephlegmator, the percentage of alcohol in the first fraction did not exceed 95.3 per cent. by weight, although, as will be seen later, the mixture of minimum boiling point really contains 95.57 per cent. of alcohol.

That the final point had not been reached was indicated by the fact that even in the seventh fractionation the strength of the alcohol steadily, although slowly, diminished as the distillation proceeded.

It was therefore hopeless to attempt to separate the mixture of constant boiling point, or, indeed, to determine its exact composition by fractional distillation. Moreover, the curve representing the relation between the boiling points and the composition of mixtures of ethyl alcohol and water is of such a form that, although the minimum boiling point is easily readable, only a rough approximation to the composition can be obtained.

With regard to the difference between the boiling points of pure alcohol and of the mixture, the results of Linebarger and of Noyes and Warfel are not in perfect agreement, but it may be concluded that this difference lies between  $0.1^{\circ}$  and  $0.15^{\circ}$ .

Our own experiments were not carried out with a view to the accurate determination of this difference, and a thermometer, graduated in whole degrees, was, in fact, employed; yet, owing to the very large number of determinations of the boiling points of alcohol-water mixtures that were made at various times, it was found possible to construct a curve which would give a fair approximation to the value under discussion. The mean of the eight observations nearest to the point of minimum temperature given in the table below would show a difference of  $0.2^{\circ}$ , although the value we should have been inclined to adopt from our curve was  $0.16^{\circ}$ , which, at any rate, does not differ seriously from the more accurate determinations referred to.

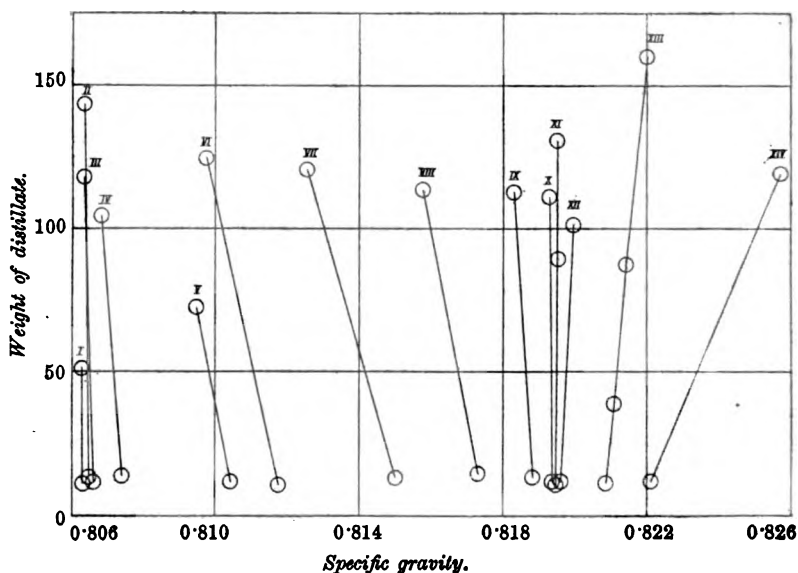
Taking the boiling point of pure alcohol as  $78.3^{\circ}$ , the observed boiling points of mixtures of nearly constant boiling point were as follows :

Sp. gr.	Pressure.	Temperature	
		observed.	corr. to 760 mm.
0.8196	758.9 mm.	78.00°	78.04°
0.8185	762.0 "	78.22	78.15
0.8194	763.6 "	78.18	78.06
0.8193	763.6 "	78.27	78.15
0.8195	756.4 "	77.95	78.07
0.8195	756.4 "	77.97	78.09
0.8195	756.4 "	77.98	78.10
0.8173	752.3 "	77.85	78.10

Mean 78.10

The value of  $dp/dt$  at the boiling point = 30.2 mm. per degree.

*Composition of the Mixture of Constant Boiling Point.*—In addition to systematic fractionation of the alcohol, numerous single distillations of alcohol of various strengths were carried out with the 18 column dephlegmator, and the sp. gr. at  $0^{\circ}/4^{\circ}$  of the first and last fractions were in each case determined. The results are shown in the diagram, the sp. gr. being plotted against the total weights of distillate. Thus, in No. X, three fractions were collected, weighing respectively 23.6, 73.4, and 27.6 grams. The sp. gr. of the first and third were determined and were taken to represent those of the distillate at the moments when  $23.6/2$  and when  $23.6 + 73.4 + 27.6/2$  grams respectively had come over.



As in the majority of cases there were only two determinations of sp. gr., a straight line has been drawn through the points, although the actual results should correctly be represented by a slightly curved line.

Starting from the left of the diagram it is evident that the curve, if obtained, would at first be represented by a vertical straight line showing constancy of composition during distillation; that the curves then actually show an increasing slope towards the left, reaching a maximum in the neighbourhood of sp. gr. 0.814; that the slope again gradually diminishes, vanishes at about sp. gr. 0.8194, then changes its direction and again shows a gradual increase. The actual experiments have not been continued, but it is clear that the slope would

again pass through a maximum, decrease and finally vanish at sp. gr. 0.99987, the liquid being then pure water.

The first two points at which the curves would become vertical straight lines represent the sp. gr. of pure alcohol and of the mixture of minimum boiling point. The method of preparation of pure alcohol has been described in the previous paper and its sp. gr. is there referred to.

By distilling various known mixtures of alcohol and water and observing whether the curves sloped to the right or left, it would be possible to get a closer and closer approximation to the mixture of minimum boiling point which distills without change of composition. It will be seen that curve X slopes to the left and curve XI to the right, and that the sp. gr. of the mixture of constant boiling point must therefore be between those (0.81936 and 0.81946) of the first fractions in these distillations.

The lines are of so nearly equal slope that it may be assumed that the required sp. gr. is 0.81941, the mean of the other two. If the two lines are produced they meet at a point between 0.81941 and 0.81942.

The sp. gr. of the mixture of constant boiling point of ethyl alcohol and water is therefore 0.81941, and the percentage of alcohol by weight that it contains is, according to Mendeléeff's data, 95.57.

### III. *n*-Propyl Alcohol and Water.

The fact that the addition of small quantities of water to *n*-propyl alcohol has the effect of lowering the boiling point was stated in 1869 by Chancel (*Compt. rend.*, 68, 662), who, from the observation that a particular mixture distilled at a constant temperature without change of composition, concluded that a definite hydrate,  $C_3H_8O, H_2O$ , was formed.

The statement that this hydrate exists is to be found in some text-books, but as a rule the point is not mentioned.

The vapour pressures of mixtures of *n*-propyl alcohol with water were investigated by Konowaloff (*loc. cit.*), who states that at 88° a mixture containing 75 per cent. by weight of the alcohol has a maximum vapour pressure, but that the composition of the mixture which exerts the maximum vapour pressure differs slightly at different temperatures. From these results, he concludes that no hydrate of propyl alcohol exists, and this conclusion seemed to be supported by the fact observed by Chancel that anhydrous potassium carbonate easily abstracts water from the mixture of constant boiling point.

Further evidence confirming Konowaloff's view was brought forward by Ramsay and Young, in 1888, in the paper already referred to.

The vapour pressures were determined by both the dynamical (Ramsey and Young) method and the statical (barometer tube) method. The differences were slight, but the pressures by the statical method were invariably a little higher. If the substance were a hydrate, or if the composition of the mixture remained constant at all temperatures, no such difference should be observed; but if the composition varied with the temperature, partial fractionation would take place by the dynamical method, somewhat higher temperatures being registered than those corresponding to the original mixture of constant boiling point obtained by distillation under the ordinary pressure.

Konowaloff states that the mixture which exerts a maximum vapour pressure is slightly poorer in alcohol at low temperatures than at high. Experiments were carried out to find whether the composition of the mixtures boiling constantly under different pressures showed a similar variation. It was found that when the mixture of constant boiling point, obtained by distillation under the ordinary pressure, was redistilled under 198.7 mm. pressure, a residue of nearly pure propyl alcohol was left. Konowaloff's result was thus fully confirmed.

Vapour density determinations above 130° in a modified Hofmann's apparatus, in which pressure and volume could be altered at will, gave the value 18.14, and, assuming that there is no combination in the state of vapour, the composition corresponding to this density would be:

<i>n</i> -Propyl alcohol.....	71.95
Water .....	28.05
	<hr/>
	100.00

Again, if no contraction took place on mixing liquid propyl alcohol and water, the volume of a gram of a mixture of this composition would be 1.1587 c.c. at 0°. The volume of a gram of the mixture of constant boiling point, obtained by distillation under the ordinary pressure, was found to be 1.1362 c.c. at 0°. If the assumption that there is no combination in the state of vapour is correct, there must be a contraction on mixing the liquids of 0.0225 c.c. per gram of the mixture, equivalent to 1.942 per cent. by volume; it was known that some contraction, at any rate, does occur.

In any case, it was clear that since the composition calculated from the sp. gr. of the liquid would differ but little from that derived from the vapour density, there could not be more than a very small amount of combination in the state of vapour.

The conclusion that the hydrate of propyl alcohol does not exist was not accepted at the time, and the paper did not appear in the Transactions. Further confirmatory evidence has now been obtained. If the hydrate of propyl alcohol existed at the ordinary temperature,

it is certain that it would not be less stable at lower temperatures; yet it was found possible to separate about two-thirds of the water by cooling the mixture of constant boiling point to  $-40^{\circ}$ . Partial crystallisation took place, and the sp. gr. of the residual liquid was 0.84145, corresponding to 9.3 per cent. of water, as against 0.88004, corresponding to 28.3 per cent.

The propyl alcohol employed in this investigation was obtained from Kahlbaum; it was carefully fractionated, and the boiling point and sp. gr. were determined, with the following results:

Pressure.	Temperature		Sp. gr. at $0^{\circ}/4^{\circ}$ .
	observed.	corr. to 760 mm.	
771.2 mm.	97.70°	97.31°	0.81931
759.5 „	97.30	97.32	0.81934

The value of  $dp/dt$  at the boiling point = 28.85 mm. per degree.

Afterwards the propyl alcohol was recovered from the mixture of constant boiling point by distillation with benzene after a portion of the water had been removed by means of potassium carbonate. Both the boiling point and the sp. gr. were slightly lowered by this treatment:

Pressure.	Temperature		Sp. gr. at $0^{\circ}/4^{\circ}$ .
	observed.	corr. to 760 mm.	
767.55 mm.	97.44°	97.18°	0.81923
763.6 „	97.32	97.20	—

These values are taken as correct.

*Mixture of Constant Boiling Point of n-Propyl Alcohol and Water.*—

In order to find whether the mixture of constant boiling point could be obtained with quite constant composition by distillation, mixtures richer both in alcohol and in water were fractionated, and the boiling points and sp. gr. of the first fractions determined.

From mixtures richer in alcohol:

Pressure.	Temperature		Sp. gr. at $0^{\circ}/4^{\circ}$ .
	observed.	corr. to 760 mm.	
756.9 mm.	87.59°	87.70°	0.88000
759.7 „	87.69	87.70	0.88002
744.2 „	87.17	87.72	0.88004

From mixtures richer in water:

747.6 mm.	87.27°	87.70°	0.88008
763.2 „	87.88	87.77	—

Mean 87.72      Mean 0.88003

The value of  $dp/dt$  at the boiling point = 28.7 mm. per degree.



These results agree well with those previously obtained by Ramsay and Young, namely, boiling point,  $87.75^{\circ}$ ; sp. gr. at  $0^{\circ}/4^{\circ}$ , 0.88015.

*Specific Gravities of Mixtures of n-Propyl Alcohol and Water.*—Known weights of pure propyl alcohol and water were mixed together, and the sp. gr. were determined with the following results:

Percentage of alcohol by weight.	Sp. gr. at $0^{\circ}/4^{\circ}$ .
94.95	0.83203
89.97	0.84307
84.87	0.85362
79.96	0.86360
74.93	0.87365
71.69	0.88004

The last sp. gr. in this table is practically identical with that of the mixture of constant boiling point obtained by distillation; the percentage composition may therefore be taken as:

n-Propyl alcohol.....	71.69
Water ... ..	28.31
	<hr/>
	100.00

This agrees very well indeed with the necessarily less accurate result, calculated from the vapour density, observed by Ramsay and Young:

n-Propyl alcohol.....	71.95
Water .....	28.05
	<hr/>
	100.00

and the conclusion previously arrived at, that there is no combination in the state of vapour, is fully confirmed. The contraction that takes place when this and other alcohols are mixed with water will be referred to later on.

#### IV. *iso*Propyl Alcohol and Water.

Three definite hydrates of *isopropyl* alcohol,  $2C_3H_7O, H_2O$ ,  $3C_3H_7O, 2H_2O$ , and  $3C_3H_7O, H_2O$  are stated in all text-books of organic chemistry to exist, and a fourth hydrate,  $C_3H_7O, H_2O$ , has also been described by Ruhemann and Carnegie (Trans., 1888, 53, 427).

Thorpe, however (Trans., 1897, 71, 920), has brought forward evidence which renders the existence of any of these hydrates very doubtful. Thorpe purified his alcohol by long continued treatment with anhydrous copper sulphate, fractionating the alcohol from time to time, and finally distilled it after boiling with lime for some time in a flask provided with a reflux condenser. The sp. gr. of two fractions

were then found to be identical, 0.7982 at  $4^{\circ}/4^{\circ}$ , and the boiling point was  $80.9-81.4^{\circ}$  at 738 mm. The boiling point under normal pressure adopted was  $82.1^{\circ}$ .

Thorpe then made mixtures of the purified alcohol and water in the proportions required to form each of the four hydrates. Three of these mixtures were allowed to evaporate over sulphuric acid until the bulk of liquid was reduced to about one-half, and through the fourth a current of air was passed until the bulk was reduced to about the same extent. In all cases, the residual alcohol was considerably stronger than at first, as shown by the diminution in the sp. gr. From these results, Thorpe concludes "that the so-called hydrates are not definite chemical compounds, but are merely mixtures of the alcohol and water."

The four "hydrates" are described by their discoverers as having the following boiling points, taking the order already given: (1) about  $80^{\circ}$ , (2)  $78-80^{\circ}$ , (3)  $81^{\circ}$ , (4)  $78-79^{\circ}$ .

As these boiling points are all lower than that of the pure alcohol, it seemed to us to be probable that isopropyl alcohol really behaves like *n*-propyl alcohol in forming with water a mixture of minimum boiling point which would distil without change of composition.

About 200 grams of isopropyl alcohol, obtained from Kahlbaum, were distilled through a five-column "evaporator" still-head. It contained, besides water, a very small amount of impurity of high boiling point and a rather larger amount of one of low boiling point. After eliminating these, relatively large quantities of two liquids, *A* and *B*, were obtained, boiling constantly at  $80.4^{\circ}$  and  $82.4^{\circ}$  respectively. The first proved to be the mixture of constant boiling point of alcohol and water; the second was nearly pure alcohol.

After the boiling points had become nearly constant, the sp. gr. of these substances were determined at the end of each fractionation with the following results:

No. of fractionation.	Sp. gr. at $0^{\circ}/4^{\circ}$ .	
	<i>A.</i>	<i>B.</i>
3 .....	—	0.80199
4 .....	—	0.80159
5 .....	0.83331	0.80144
6 .....	0.83356	—
7 .....	0.83361	—

It will be seen that the sp. gr. of *A* shows a gradual rise, that of *B* a gradual fall, both tending finally to become constant.

The fraction *B* was boiled for  $2\frac{1}{2}$  hours with barium oxide in a reflux apparatus and was then distilled. Its sp. gr. at  $0^{\circ}/4^{\circ}$  was now 0.80137. This agrees well with Thorpe's value, which, reduced by means of Zander's formula, would be 0.8014 at  $0^{\circ}/4^{\circ}$ .

It will be seen from these results that although the boiling points of the two substances differ by only two degrees it was found possible to separate the alcohol in a very nearly pure state, and it was later found that the composition of *A* was identical with that of the mixture of constant boiling point obtained by the distillation of more dilute isopropyl alcohol.

The alcohol was subsequently recovered from the mixture of constant boiling point by distillation with benzene, and it was evidently obtained still drier by this process than by heating with barium oxide, for the sp. gr. at  $0^{\circ}/4^{\circ}$ , 0.80120, was slightly lower, and the boiling point,  $82.44^{\circ}$ , was slightly higher. These values are taken as correct.

Seventy grams of the mixture of constant boiling point (*A*) and 20 grams of water were distilled together through the "evaporator" still-head, and the sp. gr. of the first fraction was found to be 0.83434 at  $0^{\circ}/4^{\circ}$ . That portion of the distillate which came over at a nearly constant temperature was redistilled and the sp. gr. of the first fraction was found to be 0.83361, which is identical with that of *A*. Thus the composition of the distillate was the same whether the original mixture was richer in alcohol or in water.

The sp. gr. of mixtures of isopropyl alcohol and water have already been determined by Thorpe (*loc. cit.*) at  $15^{\circ}/15^{\circ}$ . The sp. gr. of the mixture of constant boiling point at  $14.6^{\circ}/4^{\circ}$ , as determined by us, was 0.82116, which at  $15^{\circ}/15^{\circ}$  would become 0.82153.

From Thorpe's tables, the percentage composition corresponding to this sp. gr. would be

Alcohol .....	88.15
Water .....	11.85
	<hr/> 100.00

A mixture of this composition was then made, using the alcohol of sp. gr. 0.80137 at  $0^{\circ}/4^{\circ}$ , and its sp. gr. at  $0^{\circ}/4^{\circ}$  was found to be 0.83297, corresponding to 0.82091 at  $15^{\circ}/15^{\circ}$ .

Assuming that the alcohol used for the mixture was dry, the composition corresponding to the sp. gr. 0.82153 at  $15^{\circ}/15^{\circ}$  would be

Alcohol .....	87.9
Water .....	12.1
	<hr/> 100.0

or allowing for the traces of water present the percentage of alcohol would be about 87.85.

It will be seen that the percentage of water in the mixture of constant boiling point is much lower than in the case of two fractions of alcohol, it is higher than in that of ethyl alcohol.

The following are the observed boiling points of *isopropyl* alcohol and of its mixture of constant boiling point with water; the alcohol was that dried by distillation with benzene:

*Alcohol.*

Pressure.	Temperature	
	observed.	corr. to 760 mm.
761.5 mm.	82.46°	82.42°
771.6 „	82.85	82.46
Mean 82.44		

*Mixture of Constant Boiling Point with Water.*

From excess of water.			From excess of alcohol.		
Pressure.	Temperature		Pressure.	Temperature	
	observed.	corr. to 760 mm.		observed.	corr. to 760 mm.
746.7 mm.	79.96°	80.41°	751.85 mm.	80.11°	80.38°
764.75 „	80.55	80.39	763.5 „	80.51	80.39
		—	761.75 „	80.46	80.40
	Mean 80.40		732.0 „	79.43	80.37
			743.4 „	79.87	80.43
			760.7 „	80.36	80.34
			770.25 „	80.66	80.31
			753.9 „	80.11	80.32
			Mean 80.37		

Value of  $dp/dt$  at the boiling point: Alcohol, 30.0 mm. per degree; alcohol-water mixture, 29.7 mm. per degree.

*V. tert. Butyl Alcohol and Water.*

It was stated by Butleroff (*Annalen*, 1872, 162, 229) that *tert.* butyl alcohol, which, like those already considered in this paper, is miscible with water in all proportions, forms a definite hydrate of the formula  $2C_4H_{10}O, H_2O$ . The hydrate was described as a liquid boiling at 80° and having the sp. gr. 0.8276 at 0°.

Two hundred and fifty grams of *tert.* butyl alcohol were obtained from Kahlbaum. At the temperature of the room, 22°, the substance consisted of fine, large crystals with a good deal of liquid. The liquid was poured off and fractionated five times with the 5-column "evaporator" still-head and a good quantity was obtained boiling quite constantly at 82.45° under a pressure of 758.4 mm., corresponding to 82.5° at 760 mm. The melting point of the best fraction was 25.25°.

Meanwhile the atmospheric temperature gradually rose from about  $22^{\circ}$  to above  $25^{\circ}$ , and small additional quantities of liquid were formed by the partial fusion of the crystals, and were drained off from time to time. Finally, about half the total quantity of residual solid was melted and poured off; its melting point was  $25.20^{\circ}$ , while that of the residue was  $25.41^{\circ}$ .

As it was clear that fractional crystallisation gave better results than fractional distillation, the former process was applied to the whole quantity of nearly pure alcohol, and the melting point was finally obtained as high as  $25.43^{\circ}$ . In carrying out the fractional crystallisation, the conditions were peculiarly favourable, for the temperature of the room, after having fallen again, gradually rose in the course of about a week from about  $22^{\circ}$  to about  $25.5^{\circ}$ .

Later on, the alcohol was recovered from the mixture of constant boiling point, which it was found to form with water, by distillation with benzene. As in the case of ethyl, *n*-propyl, and isopropyl alcohols, the purest specimen was obtained by this method, the melting point being  $25.53^{\circ}$  as against  $25.43^{\circ}$ , and the boiling point  $82.60^{\circ}$  under a pressure of 761.4 mm., corresponding to  $82.55^{\circ}$  at 760 mm., as against  $82.5^{\circ}$  at normal pressure.

The sp. gr. could not be determined at  $0^{\circ}$ , owing to solidification; that of the recrystallised specimen was found to be  $0.78560$  at  $20^{\circ}/4^{\circ}$ , whilst that of the specimen dried by distillation with benzene was  $0.78553$  at  $20^{\circ}/4^{\circ}$ .

The sp. gr. of the pure alcohol and of mixtures with water were actually determined at temperatures as near as convenient to  $20^{\circ}$  and  $25^{\circ}$ , and the values obtained were corrected to these temperatures on the assumption that the sp. gr. is a linear function of the temperature over this small range:

*Sp. gr. of Mixtures of tert. Butyl Alcohol and Water.*

Percentage of alcohol. by weight.	Sp. gr. at	
	$20^{\circ}$ .	$25^{\circ}$ .
100	0.78553	0.78056
97.36	0.79128	0.78653
94.24	0.79878	0.79415
90.58	0.80718	0.80268
86.00	0.81820	0.81364
80.42	0.83146	0.82703
73.25	0.84832	0.84405

*Mixture of Constant Boiling Point with Water.*—Numerous distillations of alcohol-water mixtures were carried out, in some cases the alcohol, in others the water, being in excess. The results are given in the following table:

From mixtures richer in water :

Pressure.	Temperature		Specific gravity	
	observed.	corr. to 760 mm.	at 0°/4°.	at 25°/4°.
757·35 mm.	79·85°	79·94°	—	—
762·2    "	80·00	79·93	—	—
758·15   "	79·84	79·90	—	—
758·7     "	79·88	79·92	—	—
757·5     "	79·83	79·91	—	—
746·45   "	79·46	79·92	—	—
747·7     "	79·51	79·93	0·83046	0·80831
748·45   "	79·53	79·92	—	—

Mean 79·92

From mixtures richer in alcohol :

				At 20°/4°.
757·5 mm.	79·83°	79·91°	—	—
748·45   "	79·53	79·92	0·83041	—
758·1     "	79·80	79·86	0·83041	0·81275

Mean 79·90

The value of  $dp/dt$  at the boiling point was 29·7 mm. per degree.

The composition of the mixture of constant boiling point was ascertained in the following manner. Curves were drawn showing the relation between the percentage molecular composition and the sp. gr. at 20° and 25° respectively. From each of these curves, the composition was read off corresponding to the sp. gr. actually observed in the case of the mixture of constant boiling point.

The percentage molecular composition was thus found to be

	Alcohol.	Water.
(a) From sp. gr. at 20° (distillate from mixture richer in alcohol) .....	64·56	35·44
(b) From sp. gr. at 25° (distillate from mixture richer in water) .....	64·62	35·38
	Mean 64·59	35·41

The percentage composition by weight calculated from the mean is

Alcohol .....	88·24
Water .....	21·76
	100·00

*tert.* Butyl alcohol shows great similarity in many respects to isopropyl alcohol, as will be seen from the following table :

	<i>tert.</i> Butyl alcohol.	<i>iso</i> Propyl alcohol.
Boiling point at 760 mm. ....	82·55°	82·44°
Sp. gr. at 20°/4° .....	0·78553	about 0·7859

*Mixture of Constant Boiling Point with Water.*

Boiling point at 760 mm. ....	79·91°	80·37°
Sp. gr. at 0°/4° .....	0·83043	0·83361
Percentage of alcohol by weight .....	88·24	87·90

VI. *iso* Butyl Alcohol and Water.

As is well known, this alcohol is miscible with water only within limits, and the behaviour of a mixture with water, on distillation, is similar to that of any other partially miscible pair of liquids.

About 350 grams of *isobutyl* alcohol, obtained from Kahlbaum, were distilled through the 18-column dephlegmator. After four fractionations, a fair quantity was obtained, with constant boiling point, but the sp. gr. of the fractions showed a slight rise. On repeating the fractionation twice, the sp. gr. fell a little on the whole, and there was still a slight rise from fraction to fraction (0·81705 to 0·81723 at 0°/4°).

The fractions within these limits were mixed together and redistilled, when the sp. gr. at 0°/4° was 0·81698; at 16·35°/4°, 0·80459.

The boiling point was determined at various times, and the following values were obtained:

Pressure.	Temperature	
	observed.	corr. to 760 mm.
746·2 mm.	107·51°	108·00°
742·0 "	107·44	108·08
738·75 "	107·31	108·07
753·25 "	107·86	108·10
753·5 "	107·86	108·09
756·4 "	107·94	108·07
766·4 "	108·26	108·03

Mean 108·06

The value of  $dp/dt$  at the boiling point was taken to be 28·0 mm. per degree.

*Composition and Boiling Point of the Alcohol-Water Mixture of Constant Boiling Point.*—A mixture of *isobutyl* alcohol and water of known composition was distilled and the weight, of distillate below the middle temperature was ascertained in order to find the composition of the mixture of constant boiling point by the method described in a separate paper (p. 752). The water was in excess:

Composition of mixture taken.		Weight below middle point.	Composition of mixture of constant boiling point.			
			Uncorrected.	Corrected.		
Alcohol	49.6	Observed	73.95	Alcohol	67.1	66.8
Water	44.7	Corrected	74.25	Water	32.9	33.2
<hr/>					<hr/>	<hr/>
94.3					100.0	100.0

*Boiling Points.*

		Pressure.	Temperature	
			observed.	corr. to 760 mm.
From mixture richer in water...	{	764.5 mm.	89.95°	89.80
		766.0 "	90.03	89.82
"	"	alcohol. 757.75 "	89.75	89.83
			Mean	89.82

$dp/dt$  at the boiling point = 28.4 mm. per degree.

The sp. gr. of a series of mixtures of *isobutyl* alcohol and water were determined at 0°/4°. The results are given in the table below :

Percentage of <i>isobutyl</i> alcohol by weight.	Sp. gr. at 0°/4°.
97.72	0.82251
95.09	0.82823
91.79	0.83492
88.53	0.84125
86.76	0.84470
84.81	0.84829

The last mixture was just saturated with water at 0°.

VII. *isoAmyl Alcohol and Water.*

About 450 grams of *amyl* alcohol, obtained from Kahlbaum, were fractionated with the 18-column dephlegmator, benzene being added at first to facilitate the removal of lower homologues.

It is well known that *amyl* alcohol obtained by fermentation is a mixture of the isomeric *isoamyl* alcohol,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , and active *amyl* alcohol,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{OH}$ .

The fractionation is not yet completed, but a sufficient quantity of one of the isomerides, presumably *isoamyl* alcohol, boiling very nearly constantly at 132.05°, has been obtained. The remainder comes over at lower temperatures.

*Composition of Mixture of Constant Boiling Point with Water.*—From mixture richer in water :



Mixture taken.		Weight below middle point.	Composition of mixture of constant boiling point.			
			Uncorrected.	Corrected.		
Alcohol	38.8	Observed	76.4	Alcohol	50.8	50.5
Water	69.5	Corrected	76.9	Water	49.2	49.5
<hr/>				<hr/>	100.0	100.0
108.3						

From mixture richer in alcohol :

Alcohol	68.3	Observed	85.65	Alcohol	50.1	50.3
Water	42.7	Corrected	85.95	Water	49.9	49.7
<hr/>				<hr/>	100.0	100.0
111.0						

The mean of the two corrected values, which agree very well together, may be taken as correct :

Alcohol .....	50.4
Water .....	49.6
	<hr/>
	100.0

#### *Boiling Points.*

Pressure.	Temperature	
	observed.	corr. to 760 mm.
755.85 mm.	95.0°	95.15°
756.3   ,,	95.0	95.15
		<hr/>
		Mean 95.15

#### VIII. *Generalisations from Results.*

In a previous paper by one of us (p. 708), it is pointed out that as the molecular weights increase the properties of the alcohols diverge from those of water and approach those of the corresponding paraffins.

Since the higher alcohols are practically insoluble in water, whilst the lowest of them, methyl alcohol, dissolves in water in all proportions with considerable contraction and evolution of heat, it may be inferred that the attraction of the alcohol molecules for those of water diminishes with rise of molecular weight, and it is natural to assume that the change would be a gradual one.

This conclusion is confirmed by the results given in the following table :

*Specific Gravities, Boiling Points, and Composition of Mixtures of Constant Boiling Point of the Alcohols with Water.*

	Boiling point (760 mm.).			Sp. gr. 0°/4°.		Percentage of alcohol in mixture.	
	Alcohol.	Mixture.	Δ.	Alcohol.	Mixture.	By weight.	Molecular.
Methyl alcohol ...	64·70	—	—	0·81000	—	—	—
Ethyl „ ...	78·30	78·15	0·15	0·80625	0·81941	95·57	89·43
isoPropyl „ ...	82·44	80·37	2·07	0·83120	0·83361	87·90	68·54
tert. Butyl „ ...	82·55	79·91	2·64	—	0·83043	88·24	64·59
n-Propyl „ ...	97·19	87·72	9·47	0·81923	0·88004	71·69	48·17
isoButyl „ ...	108·06	89·82	18·24	0·81698	{ two layers	66·80	32·86
isoAmyl „ ...	132·05	95·15	36·90	—	„	50·40	17·21

Comparing the three normal primary alcohols, methyl, ethyl, and propyl, it will be seen that the first does not form a mixture of constant boiling point with water at all, whilst the difference in boiling point between the alcohol and the mixture of constant boiling point is much smaller in the case of ethyl than of propyl alcohol. Again, the percentage of alcohol in the mixture of constant boiling point is much higher in the case of ethyl than of *n*-propyl alcohol.

The table further brings out the influence of constitution on the properties of the alcohols.

That the boiling point of a paraffin or alkyl derivative containing an *iso*-group is lower than that of the normal isomeride is well known, as is also the fact that a tertiary alcohol boils at a much lower temperature than the isomeric primary compound.

The alcohols are arranged in the table in the order of their boiling points, and it will be seen that the same order is followed both as regards the difference in boiling point between the alcohol and its water-mixture of constant boiling point and also as regards the molecular percentage of alcohol in the mixture.

### IX. Contraction on Mixing with Water.

The contraction that takes place on mixing the various alcohols with water was calculated from the sp. gr. of a series of mixtures of known composition in each case.

The required data for methyl, ethyl, and isopropyl alcohols were already available [methyl alcohol, Dittmar and Fawsitt (*loc. cit.*);

ethyl alcohol, Mendeléeff (*loc. cit.*) ; isopropyl alcohol, Thorpe (*loc. cit.*), and determinations were therefore only made with *n*-propyl, *tert.* butyl, and isobutyl alcohols.

In the case of methyl and of ethyl alcohol, data are given at  $0^{\circ}/4^{\circ}$ , but for isopropyl alcohol only at  $15^{\circ}/15^{\circ}$ . In order to find whether the contraction differed much at different temperatures, the data given by Dittmar and Fawsitt for methyl alcohol at  $15.6^{\circ}/4^{\circ}$  were also made use of. It will be seen from the following table that the contractions are nearly the same at the two temperatures, and it was therefore not a matter of importance that the comparison had to be made at different temperatures.

The plan adopted was to calculate the volumes of a gram from the observed sp. gr., and also the theoretical volumes of a gram, supposing that no contraction occurred on mixing (see p. 737). The percentage contractions are given in the following table :

*Percentage Contraction.*

Molecular percentage of alcohol.	Methyl alcohol.		Ethyl alcohol.	isoPropyl alcohol.	<i>tert.</i> Butyl alcohol.		<i>n</i> -Propyl alcohol.	isoButyl alcohol.
	$15.56^{\circ}$ .	$0^{\circ}$ .	$0^{\circ}$ .	$15^{\circ}$ .	$20^{\circ}$ .	$25^{\circ}$ .	$0^{\circ}$ .	$0^{\circ}$ .
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
95	0.44	0.44	0.38	0.13	0.06	0.07	0.27	0.15
90	0.88	0.84	0.74	0.36	0.17	0.19	0.43	0.28
85	1.28	1.28	1.06	0.57	0.30	0.32	0.62	0.40
80	1.68	1.68	1.38	0.79	0.41	0.47	0.80	0.51
75	2.04	2.04	1.69	1.01	0.55	0.59	0.97	0.60
70	2.40	2.39	1.99	1.28	0.71	0.74	1.12	0.72
65	2.69	2.70	2.29	1.43	0.85	0.90	1.25	0.81
60	2.97	2.98	2.56	1.65	1.02	1.05	1.42	0.90
55	3.19	3.22	2.83	1.85	1.21	1.25	1.57	—
50	3.42	3.45	3.09	2.05	1.40	1.42	1.71	—
45	3.54	3.60	3.34	2.20	1.60	1.63	1.85	—

It will be noticed that of the six alcohols examined, four are primary—methyl, ethyl, and *n*-propyl alcohols being derived from normal paraffins, isobutyl alcohol from an isoparaffin ; of the other two, isopropyl alcohol is a secondary alcohol derived from a normal paraffin, whilst *tert.* butyl alcohol is a tertiary alcohol derived from an isoparaffin.

In studying the properties of these alcohols, account must therefore be taken both of the constitution of the paraffins from which they are derived, and also of the position of the hydroxyl group. Of these two factors, the latter seems to have the greater influence so far as contraction on mixing with water is concerned, for, with the four primary

*Volumes of a Gram.*

Mole- cular-per- centage of alcohol.	Methyl alcohol.		Ethyl alcohol.		isoPropyl alcohol.		tert. Butyl alcohol.		n-Propyl alcohol.		isoButyl alcohol.	
	0°.		0°.		15°.		20°.		25°.		0°.	
	15.56°.											
	Ob- served.	Calcu- lated.	Ob- served.	Calcu- lated.	Ob- served.	Calcu- lated.	Ob- served.	Calcu- lated.	Ob- served.	Calcu- lated.	Ob- served.	Calcu- lated.
100	1.2565	1.2565	1.2343	1.2403	1.2665	1.2730	1.2730	1.2811	1.2207	1.2207	1.2240	1.2240
95	1.2486	1.2491	1.2276	1.2355	1.2596	1.2688	1.2696	1.2766	1.2145	1.2172	1.2194	1.2212
90	1.2306	1.2415	1.2100	1.2203	1.2523	1.2568	1.2637	1.2714	1.2083	1.2135	1.2147	1.2181
85	1.2176	1.2334	1.1977	1.2132	1.2449	1.2520	1.2581	1.2656	1.2020	1.2096	1.2099	1.2148
80	1.2044	1.2250	1.1853	1.2055	1.2370	1.2469	1.2523	1.2575	1.1956	1.2053	1.2050	1.2112
75	1.1913	1.2161	1.1730	1.1974	1.2288	1.2413	1.2458	1.2527	1.1890	1.2006	1.2000	1.2072
70	1.1780	1.2069	1.1605	1.1869	1.2200	1.2352	1.2387	1.2475	1.1821	1.1955	1.1943	1.2029
65	1.1648	1.1970	1.1480	1.1798	1.2110	1.2285	1.2310	1.2416	1.1750	1.1899	1.1884	1.1981
60	1.1515	1.1868	1.1355	1.1704	1.2011	1.2212	1.2225	1.2351	1.1671	1.1839	1.1820	1.1927
55	1.1384	1.1759	1.1231	1.1605	1.1908	1.2133	1.2131	1.2280	1.1596	1.1772	—	—
50	1.1248	1.1646	1.1104	1.1466	1.1797	1.2044	1.2028	1.2199	1.1508	1.1698	—	—
45	1.1119	1.1527	1.0983	1.1393	1.1680	1.1943	1.1915	1.2109	1.1498	1.1615	—	—

alcohols, the percentage contraction decreases in the same order as the boiling points rise and as the molecular percentages of alcohol in the mixtures of constant boiling point diminish; but with the secondary and tertiary alcohols examined, the order depends on the concentration, and it is only with large quantities of water that *isopropyl* alcohol takes its proper place, whilst for mixtures rich in *isopropyl* alcohol, and for all the *tert.* butyl alcohol mixtures within the limits of the table, the percentage contraction is very low.

### X. Heat Changes on Mixing with Water.

In order to carry out a complete investigation of these changes, a much larger amount of material would be required than we had at our disposal except in the case of methyl alcohol. It was thought worth while, however, to make an approximate comparison of the heat changes produced by mixing the alcohols with water, taking the same molecular proportions in each case.

The alcohol and water were mixed together in a small, round-bottomed flask in the proportion of 60 mols. of alcohol to 40 of water, the total weight in each case being about 30 grams.

The initial temperatures of the alcohol and of the water, which were identical, or nearly so, and the final temperature of each mixture are given in the table below, together with the difference between the final temperature and the mean of the initial temperatures.

#### Temperatures.

	Water.	Alcohol.	Mean.	Mixture.	Δ.
Methyl alcohol .....	21·7°	21·7°	21·7°	29·55°	+7·85°
Ethyl „ .....	22·2	22·35	22·3	25·25	+2·95
<i>tert.</i> Butyl „ .....	26·25	26·25	26·25	25·20	-1·05
<i>n</i> -Propyl „ .....	22·7	22·7	22·7	21·55	-1·15
<i>iso</i> Butyl „ .....	22·3	22·3	22·3	19·15	-3·15

No experiment was made with *isopropyl* alcohol, as the quantity at our disposal was very small, or with *isoamyl* alcohol on account of its slight solubility, but it will be seen that in the case of the other alcohols the evolution of heat diminishes, or the absorption of heat increases, as the boiling points of the alcohols rise.

With a large excess of water, evolution of heat was observed in every case, and rough experiments were made to find the maximum rise of temperature for each alcohol. The results are appended.

	Approximate maximum rise of temperature.
Methyl alcohol.....	8.5°
Ethyl       ,, .....	6.5
<i>tert.</i> Butyl ,, .....	4.0
<i>n</i> -Propyl   ,, .....	4.0
<i>iso</i> Butyl   ,, .....	1.0

Here again the order is the same as that of the boiling points.

With regard to the general question whether the mixtures of constant boiling point of the alcohols with water are definite hydrates or not, in addition to the special arguments against the existence of such hydrates advanced in the case of *n*-propyl and of *isopropyl* alcohols, it seems sufficient to point to the fact that in none of the cases examined do the number of molecules of alcohol and water in the mixture bear a simple ratio to each other.

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## LXXV.—*The Properties of Mixtures of the Lower Alcohols with Benzene and with Benzene and Water.*

By SYDNEY YOUNG, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

In a previous paper (p. 708), it has been pointed out that since the monohydric aliphatic alcohols may be regarded on the one hand as hydroxyl derivatives,  $C_nH_{2n+1}(OH)$ , of the paraffins, and on the other as alkyl derivatives,  $(C_nH_{2n+1})O \cdot H$ , of water, their properties should approach those of the corresponding paraffins and recede from those of water as the molecular weight increases. The second point has been considered in the last paper (p. 717), and we now propose to describe experiments which bring out the relationship of the alcohols to the paraffins and other hydrocarbons.

Owing to the fact that the lowest paraffins are gaseous under ordinary conditions, it is not possible to deal experimentally with mixtures of these paraffins with the corresponding alcohols. There are also very few of the paraffins which can easily be obtained in a pure state. *n*-Hexane might, indeed, be employed, as when prepared from pure propyl iodide and sodium it is readily purified, but it is too expensive a material to be used in large quantities. Benzene, however, was found to behave in a similar manner to *n*-hexane, and it was therefore made use of in the majority of the experiments.

In order to obtain satisfactory results, it is necessary to employ a very efficient still-head. In all the experiments described in this paper, with the exception of those with ethyl alcohol, a 5-column "evaporator" still-head was used. For ethyl alcohol mixtures, the 18-column Young and Thomas dephlegmator was employed.]

A few experiments were made with *n*-hexane and ethyl alcohol, the results of which are given below. Mixtures of the carefully dried alcohol and hexane were distilled together and the following boiling points were observed:

Pressure.	Temperature	
	observed.	corr. to 760 mm.
740.1 mm.	57.91°	58.64°
748.85 "	58.33	58.74
764.4 "	58.83	58.67
Mean 58.68		

$dp/dt$  at the boiling point = 27.1 mm. per degree.

In two cases, known weights were taken, the alcohol being in excess, and the weights of distillate below the temperature midway between the boiling points of the mixture of constant composition and of alcohol were ascertained. From these results, the composition of the mixture of constant boiling point was calculated by the method described in the next paper, and was found to be:

Alcohol .....	21.0 per cent.
Hexane .....	79.0 "
	<hr/> 100.0 "

When ethyl alcohol, *n*-hexane, and water are distilled together, a mixture of the three substances comes over at a constant temperature. One determination of this temperature was made, and it was found to be 56.60° at 760 mm., or 2.08° lower than the boiling point of the binary alcohol-hexane mixture, 4.95° lower than that of the hexane-water mixture, and 21.55° lower than that of the alcohol-water mixture. These results are not very different from those observed with benzene, but from the point of view of the separation of water from alcohol they are less favourable.

### I. Methyl Alcohol.

*Methyl Alcohol and Benzene.*—Known weights of pure methyl alcohol and benzene were distilled together; in one case, M, the alcohol, and in the other, N, the benzene, was in large excess over that which was found to be required for the mixture of constant boiling point. The

weight of distillate below the middle temperature between the boiling point of the mixture of constant composition and that of the pure liquid in excess was ascertained in each case, in order to calculate the composition of the mixture of constant boiling point by the method described in the next paper (p. 752).

*Boiling points :*

Pressure.	Temperature			Composition of mixture of constant boiling point.		
	obs.	corr. to 760 mm.		M	N	Mean
M. 765.05 mm.	58.53°	58.35°	Alcohol	39.5	39.6	39.55
N. 762.3   ,,	58.41	58.33	Benzene	60.5	60.4	60.45
				100.0	100.0	100.00

$dp/dt$  at the boiling point = 28.1 mm. per degree.

*Methyl Alcohol, Benzene, and Water.*—A mixture of the three substances was distilled, but the distillate was clear and the boiling point was practically identical with, and certainly not lower than, that of the alcohol-benzene mixture. In this case, therefore, no ternary mixture of minimum boiling point is formed, and the water, instead of coming over, as in the case of ethyl alcohol, in the lowest fraction, accumulates in the still.

## II. Ethyl Alcohol.

The application of the results of this investigation to the preparation of absolute alcohol from strong spirit have been described in the paper which forms the first of this series (p. 707).

*Ethyl Alcohol and Benzene.*—Three determinations of boiling point were made, the original mixture in two cases, *A* and *B*, containing excess of alcohol, in the third, *C*, excess of benzene.

	Pressure.	Temperature	
		observed.	corr. to 760 mm.
A.	745.3 mm	67.71°	68.26°
B.	753.3   ,,	67.93	68.18
C.	765.2   ,,	68.49	68.29

Mean 68.24

$dp/dt$  at the boiling point = 26.6 mm. per degree.

In the mixture *C*, the benzene was only in slight excess, and the sp. gr. of the distillate was determined in order to ascertain the composition of the mixture of constant boiling point.

The observed sp. gr., 0.86740, at 0°/4° corresponds to 32.36 per cent. of alcohol, assuming that no change of volume occurs on mixing the



two liquids. In order to test this point, the sp. gr. of a mixture containing 7.850 grams of alcohol and 17.259 grams of benzene, or 31.26 per cent. of alcohol, was determined, and was found to be 0.86851. The volume of a gram corresponding to this sp. gr. is 1.1514, and that calculated from the composition on the assumption that there is no change of volume on mixing is also 1.1514. It may therefore be assumed that there is no appreciable contraction or expansion.

The composition was also determined by distilling a known mixture containing a large excess of benzene, and weighing the distillate which came over below the middle temperature. As will be seen, the agreement is excellent :

	From sp. gr.	By distillation.
Alcohol.....	32.36	32.45
Benzene .....	67.64	67.55
	<u>100.00</u>	<u>100.00</u>

*Ethyl Alcohol, Benzene, and Water.*—In the course of the preparation of pure alcohol by distillation of strong spirit with benzene, a large number of determinations of the boiling point of the ternary mixture were made. In these cases, alcohol was of course the final product, but later on a few determinations were made with mixtures from which (1) water, (2) benzene was finally left in the still. The results are given below :

*Residue in Still.*

Alcohol.			Water.			Benzene.		
Press.	Temperature.		Press.	Temperature.		Press.	Temperature.	
	Obs.	Corr.		Obs.	Corr.		Obs.	Corr.
mm.			mm.			mm.		
764.7	65.02°	64.85°	761.2	64.94°	64.90°	763.2	64.99°	64.87°
753.7	64.62	64.85	762.6	64.97	64.87	764.5	65.00	64.84
758.8	64.62	64.85	763.8	65.02	64.88			
757.35	64.77	64.87					Mean...	64.85
762.8	64.95	64.85		Mean...	64.88			
760.2	64.85	64.85						
753.1	64.62	64.87						
754.5	64.65	64.85						
764.8	65.02	64.84						
	Mean...	64.85						

Final mean 64.86

$dp/dt$  at the boiling point = 27.3 mm. per degree.

The ternary mixture is turbid, and separates on standing into two layers, of which the lower, consisting of dilute alcohol with a small amount of dissolved benzene, is by far the smaller. When the alcohol is in large excess in the original mixture and the benzene more than would be sufficient to take over all the water if the separation were complete, the liquid tends to separate into the three fractions: (1) benzene-alcohol-water, (2) benzene-alcohol, (3) alcohol.

In this case, the distillate remains turbid until the temperature midway between the boiling points of (1) and (2) is reached. After the temperature begins to rise above  $64.86^{\circ}$ , the distillate becomes richer in alcohol and poorer in water, and the alcohol-water layer therefore becomes lighter. If the original mixture is poor in water, and especially if the temperature of the room is low, it may happen that the alcohol-water layer has the same, or even a lower, specific gravity than the benzene layer, and we have, in fact, observed the two layers change places as the temperature altered.

*Composition of the Ternary Mixture.*—A direct determination of the composition of the ternary mixture was made in the following manner. A considerable quantity, obtained by distillation of mixtures rich in alcohol was redistilled, and 141.3 grams of the mixture were placed in a separating funnel, and water was added to separate the benzene more completely. The aqueous alcohol, containing a minute quantity of dissolved benzene, was run off, and the residual benzene was washed three times with small quantities of water to extract completely the dissolved alcohol, the washings being added to the main quantity of dilute alcohol. The washed benzene was poured into a tared flask and was found to weigh 104.3 grams. The dilute alcohol was then distilled until the temperature rose to  $78^{\circ}$ , and the turbid distillate was transferred to the separating funnel, which still contained a very small amount of benzene. This small quantity of turbid mixture was then treated with water as before, and the washed benzene separately weighed and found to amount to 0.3 gram.

The washings from this benzene were added to the original quantity of dilute alcohol, and the whole was distilled until the temperature rose to  $100^{\circ}$ . The distillate was no longer turbid even at first, and could not have contained more than a trace of benzene. The weight of distillate was 68.0 grams, and its specific gravity at  $0^{\circ}/4^{\circ}$  was 0.95201, corresponding to 38.5 per cent. of alcohol; the weight of alcohol was, therefore, 26.2 grams. The weight of water, calculated by difference, was 10.5 grams. The percentage composition of the ternary mixture is therefore:

Benzene.....	74.1
Alcohol .....	18.5
Water .....	7.4
	<hr/>
	100.0

The distillation method may be employed to determine the composition of the ternary mixture if that of the original mixture and that of the binary mixture of constant boiling point are known.

As there are three possible binary mixtures, and we may have alcohol, water, or benzene left in the still at the end of the distillation, it follows that when all three fractions are actually formed there are six possible methods of separation, according to the relative quantities of the components in the original mixture.

In practice, five of these cases are available for the determination of the composition of the ternary mixture, the sixth being excluded on account of the very small difference between the boiling point of the alcohol-water mixture and that of pure alcohol.

The other five cases were actually investigated, and details of the results are given in the separate paper on "Fractional Distillation as a Method of Quantitative Analysis" (p. 752). It will be sufficient here to give the mean percentages, calculated from the five determinations, which agree very well with those obtained directly :

	By distillation.	Directly determined.
Benzene.....	74.3	74.1
Alcohol .....	18.2	18.5
Water .....	7.5	7.4
	<hr/>	<hr/>
	100.0	100.0

### III. *iso*Propyl Alcohol.

*iso*Propyl Alcohol and Benzene.—*iso*Propyl alcohol and benzene form a mixture of minimum boiling point the composition of which was determined by distillation of a known mixture. The details are as follows :

Mixture taken.	Weight below middle point.*	Composition of mixture of constant boiling point. Corrected.
Alcohol 21.3	Observed 63.8	Alcohol 33.3
Benzene 65.35	Corrected 64.1	Benzene 66.7
	<hr/>	<hr/>
	86.65	100.0

\* By "middle point" is to be understood the temperature midway between the boiling points of the two liquids, whether pure substances or mixtures of constant

The benzene was in excess in the original mixture.

Four mixtures of *isopropyl* alcohol and benzene were distilled, three containing alcohol and one benzene in excess. The boiling points are as follows :

Alcohol in excess.			Benzene in excess.		
Pressure.	Temperature		Pressure.	Temperature	
	obs.	corr. to 760 mm.		obs.	corr. to 760 mm.
763·5	72·01°	71·88°	765·4	72·11°	71·91°
733·3	70·91	71·91			
772·2	72·43	71·97			
Mean 71·92			General mean 71·92°.		

$dp/dt$  at the boiling point = 26·6 mm. per degree.

*isoPropyl Alcohol, Benzene, and Water.*—Having only a small quantity of pure alcohol at our disposal, the alcohol-water mixture of constant boiling point was employed, and its composition determined as follows :

Mixture taken.		Corresponding to	
Alcohol-water mixture	27·45	Alcohol.....	24·13
Benzene .....	86·05	Benzene.....	86·05
Water .....	2·95	Water .....	6·27
116·45		116·45	

The benzene was in greatest excess, and the distillate tended to separate into (1) the ternary mixture ; (2) the alcohol-benzene mixture ; (3) benzene :

	Obs.		Composition of ternary mixture.	
	Obs.	Corr.		Corr.
Weight below first middle point	83·3	83·6	Alcohol	18·7
Weight below second middle point	25·4	25·5	Benzene	73·8
			Water	7·5
			100·0	

It will be seen that the composition of the alcohol-benzene and of the alcohol-benzene-water mixtures of constant boiling point is nearly the same in the case of ethyl and of *isopropyl* alcohols.

For the determination of the boiling point, five mixtures were distilled ; in one case benzene and in the other four alcohol was the final product left in the still.

boiling point, into which the original mixture tends to separate, or, in the case of a more complex mixture, the temperature midway between the boiling points of any two consecutive fractions of constant boiling point.

*Residue in still:*

Benzene.			Alcohol.		
Pressure.	Temperature		Pressure.	Temperature	
	obs.	corr. to 760 mm.		obs.	corr. to 760 mm.
747.0 mm.	65.99°	66.47°	752.6 mm.	66.29°	66.55°
			757.05 "	66.44	66.55
			751.1 "	66.17	66.50
			753.9 "	66.24	66.46
General mean		66.51			
Mean 66.51					

$dp/dt$  at the boiling point = 27.0 mm. per degree.

IV. *tert.* Butyl Alcohol.

*tert.* Butyl Alcohol and Benzene.—*tert.* Butyl alcohol and benzene form a mixture of minimum boiling point the composition of which was determined by distillation of a known mixture. The details are as follows :

Mixture taken.		Weight below middle point.	Composition of mixture of constant boiling point. Corrected.
Alcohol	33.8	Observed 92.0	Alcohol 36.6
Benzene	120.0	Corrected 92.3	Benzene 63.4
153.8			100.0

The benzene was in excess in the original mixture.

For the determination of the boiling point, two mixtures of *tert.* butyl alcohol and benzene were distilled ; the benzene was in excess in both cases :

Pressures.	Temperature	
	observed.	corr. to 760 mm.
755.0 mm.	73.77°	73.96°
760.25 "	73.95	73.94
Mean		73.95°

$dp/dt$  at the boiling point = 26.0 mm. per degree.

*tert.* Butyl Alcohol, Benzene, and Water.—As in the case of *isopropyl* alcohol, the alcohol-water mixture of constant boiling point was used, but no additional water was required. The composition was determined as follows :

Mixture taken.		Corresponding to	
Alcohol-water mixture	117.5	Alcohol .....	103.7
Benzene.....	145.0	Benzene.....	145.0
		Water .....	13.8
262.5			262.5

The alcohol was in largest excess, and the distillate tended to separate into (1) the ternary mixture; (2) the alcohol-benzene mixture; (3) alcohol :

	Obs.	Corr.	Composition of ternary mixture.	Corr.
Weight below first middle point	169.3	169.7	Alcohol	21.4
Weight below second middle point	39.9	40.0	Benzene	70.5
			Water	8.1
				<hr/> 100.0

For the determination of the boiling point, two mixtures were distilled; in both, the alcohol was the final product, but in one the second fraction consisted of the alcohol-water mixture, in the other of the alcohol-benzene mixture :

Pressure.	Temperature	
	observed.	corr. to 760 mm.
756.3 mm.	67.16°	67.30°
757.55 ,,	67.20	67.30
		<hr/> Mean 67.30

$dp/dt$  at the boiling point = 27.0 mm. per degree.

#### V. *n*-Propyl Alcohol.

*n*-Propyl Alcohol and Benzene.—Known weights of pure *n*-propyl alcohol and benzene were distilled together; in one case, M, the alcohol, and in the other, N, the benzene, was in excess over that which was found to be required for the mixture of constant boiling point. Details are given in the paper which follows, and it will be sufficient here to give the corrected values :

	Composition of mixture of constant boiling point.		
	M.	N.	Mean.
Alcohol .....	16.9	16.9	16.9
Benzene.....	83.1	83.1	83.1
	<hr/> 100.0	<hr/> 100.0	<hr/> 100.0

#### Boiling points :

Alcohol in excess.			Benzene in excess.		
Pressure.	Temperature		Pressure.	Temperature	
	obs.	corr. to 760 mm.		obs.	corr. to 760 mm.
769.6 mm.	77.55°	77.17°	766.4 mm.	77.39°	77.13°
761.0 ,	77.10	77.06			
		<hr/> Mean 77.11			<hr/> General mean 77.12°.

$dp/dt$  at the boiling point = 25.0 mm. per degree.

*n-Propyl Alcohol, Benzene, and Water.*—The mixture was made in the same manner as with *tert.* butyl alcohol, and its composition determined as follows :

Mixture taken.		Corresponding to	
Alcohol-water mixture...	30.0	Alcohol.....	21.55
Benzene.....	120.1	Benzene... ..	120.10
	<hr/>	Water .....	8.45
	150.1		<hr/>
			150.10

The alcohol was in greatest excess, and the distillate tended to separate into (1) the ternary mixture, (2) the alcohol-benzene mixture, (3) alcohol :

	Obs.	Corr.	Composition of ternary mixture.	
				Corr.
Weight below first middle point...	98.1	98.4	Alcohol....	9.0
Weight below second middle point	46.9	47.0	Benzene...	82.4
			Water ...	8.6
				<hr/>
				100.0

The boiling points of the above mixture and of another which separated into similar fractions were determined :

Pressure.	Temperature	
	obs.	corr. to 760 mm.
770.25 mm.	68.81°	68.42°
761.2   ,,	68.60	68.55
		<hr/>
		Mean 68.48

$dp/dt$  at the boiling point = 26.3 mm. per degree.

#### VI. *iso*Butyl Alcohol.

*iso*Butyl Alcohol and Benzene.—The difference between the boiling points of the mixture of constant composition and of benzene was too small to admit of the distillation being stopped accurately at the middle point, and it was therefore only feasible to determine the composition by distilling a mixture containing excess of alcohol :

Mixture taken.	Weight below middle point.		Composition of mixture of constant boiling point.	
	Obs.	Corr.		Corr.
Alcohol 35.35	108.1	108.5	Alcohol	9.3
Benzene 98.45			Benzene	90.7
				<hr/>
				100.0

*Boiling point :*

Pressure.	Temperature	
	obs.	corr. to 760 mm.
762.25 mm.	79.93°	79.84°

$dp/dt$  at the boiling point = 24.0 mm. per degree.

*isoButyl Alcohol, Benzene, and Water.*—On distilling a mixture of alcohol, benzene, and water, the benzene-water mixture of constant boiling point came over first. In a quantitative experiment, 6.5 grams of water were added to about 130 grams of the alcohol-benzene mixture, the proportions being such that the liquid should separate into (1) benzene-water, (2) alcohol-benzene, (3) alcohol. The boiling point of the first fraction was as follows :

Pressure.	Temperature		
	observed.	corr. to 760 mm.	calc. from vapour pressures.*
746.35 mm.	68.78°	69.31°	69.25°

*Composition of first fraction :*

Weight below first middle point.		Percentage of water in first fraction.	
obs.	corr.	corr.	calc. from vapour pressures and vapour densities.
73.05	73.35	8.86	8.83

The results obtained proved conclusively that no ternary mixture is formed in this case, and that the mixture of minimum boiling point is identical with that obtained by distilling merely benzene and water together.

VII. *isoAmyl Alcohol.*

*isoAmyl Alcohol and Benzene.*—A mixture of 26.6 grams of *isoamyl* alcohol with 85.7 grams of benzene was distilled. The temperature rose at once to 80.27°, or slightly higher than the boiling point of pure benzene. It appeared, therefore, that no mixture of constant boiling point was being formed, and the distillate was collected below the middle temperature between the boiling points of benzene and *isoamyl* alcohol :

Weight below middle point (106.1°).		Percentage composition of mixture.		
obs.	corr.	Found.		Taken.
		uncorr.	corr.	
85.55	85.85	Alcohol ... 23.8	23.6	23.7
		Benzene ... 76.2	76.4	76.3
		100.0	100.0	100.0

It is thus clear that no mixture of minimum boiling point is formed

\* Benzene and water being practically non-miscible.



and that both pure benzene and pure *iso*amyl alcohol may be separated from the mixture by fractional distillation.

*iso*Amyl Alcohol, Benzene, and Water.—As in the case of *isobutyl* alcohol, no ternary mixture is formed, but the mixture of benzene and water of constant boiling point comes over first.

### VIII. Tabulation of Data.

For the sake of convenience, the boiling points and the composition of the alcohol-benzene and of the alcohol-benzene-water mixtures of constant boiling point are tabulated below :

#### *Alcohol-Benzene.*

Name.	Boiling point (760 mm.).		Percentage of alcohol in mixture.	
	Alcohol.	Mixture.	By weight.	Molecular.
Methyl alcohol .....	64·70°	58·34°	39·55	61·4
Ethyl       " .....	78·30	68·24	32·36	44·8
<i>iso</i> Propyl   " .....	82·44	71·92	33·3	39·3
<i>tert.</i> Butyl " .....	82·55	73·95	36·6	37·7
<i>n</i> -Propyl   " .....	97·19	77·12	16·9	20·9
<i>iso</i> Butyl   " .....	108·06	79·84	9·3	9·71
<i>iso</i> Amyl     " .....	132·05	—	—	—

It will be seen that the boiling points of the mixtures and the molecular percentages of alcohol in them follow the same order as the boiling points of the pure alcohols.

#### *Alcohol-Benzene-Water.*

Name.	Boiling point at 760 mm.	Composition of mixture.					
		Weight percentage.			Molecular percentage.		
		Alcohol.	Benzene.	Water.	Alcohol.	Benzene.	Water.
Methyl alcohol ...	—	—	—	—	—	—	—
Ethyl       " ...	34·86°	18·5	74·1	7·4	22·8	53·9	23·3
<i>iso</i> Propyl   " ...	66·51	18·7	73·8	7·5	18·6	56·5	24·9
<i>tert.</i> Butyl " ...	67·30	21·4	70·5	8·1	17·5	55·0	27·5
<i>n</i> -Propyl   " ...	68·48	9·0	82·4	8·6	8·9	62·8	28·3
<i>iso</i> Butyl   " ...	—	—	—	—	—	—	—
<i>iso</i> Amyl     " ...	—	—	—	—	—	—	—

Referring first to the table of alcohol-water boiling points in the previous paper (p. 735), it will be seen that as the boiling points of the alcohols fall there is a rapid and fairly regular diminution in the differences between the boiling points of the alcohols and of the respective alcohol-water mixtures of constant boiling point, and as this difference has fallen in the case of ethyl alcohol to  $0.15$ , it is clear that with methyl alcohol, if a binary mixture of constant boiling point could exist, it would boil somewhat higher than pure methyl alcohol, but, of course, a mixture of constant boiling point could not be formed under such conditions.

As regards the alcohol-benzene mixtures of constant boiling point, passing from methyl to *isobutyl* alcohol the boiling points are in the same order as those of the alcohols, those of *isobutyl* alcohol and benzene being very near together. If *isoamyl* alcohol and benzene formed a mixture of constant boiling point, it would boil higher than benzene; it cannot therefore exist, and it may be stated that no alcohol which distills at a higher temperature than *isoamyl* alcohol would form a mixture of constant boiling point with benzene.

By reference to the table of the alcohol-water boiling points in the previous paper and to the tables of alcohol-benzene and of alcohol-benzene-water boiling points given above, it will be seen that taking the four alcohols, ethyl, *isopropyl*, *tert.*butyl, and *n*-propyl, there is a rise of  $9.57^{\circ}$  in the case of the alcohol-water mixtures,  $8.88^{\circ}$  with the alcohol-benzene mixtures, but only  $3.62^{\circ}$  in the case of the ternary mixtures.

From the last table, it would appear that the boiling point of the methyl alcohol ternary mixture, if it existed, would be not lower than  $60^{\circ}$ , but the boiling point of the methyl alcohol-benzene mixture is  $58.34^{\circ}$  and as this is lower than that of either the hypothetical ternary mixture, the binary benzene-water mixture, or the alcohol itself, the alcohol-benzene mixture is the one which must come over in the first fraction.

With regard to *isobutyl* alcohol, the ternary mixture, if formed, would evidently have a boiling point above  $69^{\circ}$  and probably above  $69.25^{\circ}$ , that of the water-benzene mixture of constant boiling point. As the boiling points of the alcohol-benzene mixture,  $79.84^{\circ}$ , and of the alcohol-water mixture,  $89.82^{\circ}$ , are both higher than  $69.25^{\circ}$ , it was a question whether the first fraction would consist of the ternary mixture or of the benzene-water mixture. The result of the distillation showed that the ternary mixture is not formed and it may be concluded that no alcohol with a higher boiling point than that of *isobutyl* alcohol would form such a mixture, and that in all such cases the first fraction would consist of benzene and water. This was actually found to be the case with *isoamyl* alcohol.

In conclusion, it may be pointed out that the behaviour on distillation of a mixture of a saturated monohydric aliphatic alcohol with benzene and water is closely related to the boiling point of the alcohol.

In the case of the lowest member of the series, methyl alcohol, the first fraction consists of the binary alcohol-benzene mixture; with *isobutyl* alcohol and all others of higher boiling point, the first fraction is the binary benzene-water mixture; as regards the alcohols of intermediate boiling point, the first fraction in the case of the four alcohols examined is the ternary mixture, but for the three alcohols, *sec.*butyl alcohol, dimethylethylcarbinol, and *tert.*butylcarbinol, the boiling points of which are intermediate between those of *n*-propyl and *isobutyl* alcohols, the question whether the first fraction would consist of the ternary mixture or the benzene-water mixture can only be decided by experiment. It seems, however, not unlikely that the ternary mixture would be formed, at any rate, with *sec.*butyl alcohol.

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## LXXVI.—*Fractional Distillation as a Method of Quantitative Analysis.*

By SYDNEY YOUNG, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

IN a paper by one of us entitled "Experiments on Fractional Distillation" (*J. Soc. Chem. Ind.*, 1900, 19, 1072), it was pointed out that the composition of a mixture of homologous substances could in many cases be ascertained with a fair degree of accuracy from the results of two or three fractional distillations with an efficient still-head, or in the case of a mixture of two components which are not difficult to separate, from the result of a single distillation.

The method depends on the following facts:—Taking first the simplest case, that of a mixture of two liquids, it is found that the weight of distillate which comes over below the middle point\* is almost exactly equal to that of the component of lower boiling point, even when the separation is very far from complete.

If the original mixture contains more than two, say  $n$ , components, the weights of these components will be very nearly equal respectively to (1) the weight of distillate below the first middle point, (2 to  $n - 1$ ) the

\* By middle point is to be understood the temperature midway between the boiling points of the two liquids, whether pure substances or mixtures of constant boiling point, into which the original mixture tends to separate; or, in the case of a more complex mixture, the temperature midway between the boiling points of any two consecutive fractions of constant boiling point.

weights of distillate between the successive middle points, ( $n$ ) the weight above the last middle point.

Only two mixtures of substances which are not homologous—methyl alcohol-water and *iso*amyl alcohol-benzene—and which separate normally into the two components, have been examined, but a considerable number of cases in which mixtures of minimum boiling point are formed have been investigated, and it has been found that such mixtures of constant boiling point behave like pure liquids. Thus, if the composition of the mixture of minimum boiling point is known, that of the original mixture may be calculated from the weight of distillate below the middle point, and, on the other hand, if the composition of the original mixture is known, that of the mixture of minimum boiling point may be calculated. The same remarks would apply to binary mixtures of maximum boiling point, such as that of formic acid and water, but so far we have not examined any such mixture.

It is obvious that there must be some loss of liquid by evaporation, which makes the weight of distillate somewhat too low. This loss will be greater as the initial boiling point is lower, and as the temperature of the room is higher. It is not proportional to the amount of liquid distilled, for a great part of the loss is caused by the saturation of the air in the flask and still-head while it is being expelled by the rising vapour. Under otherwise similar conditions, the loss is therefore roughly proportional to the volume of air in the still and still-head, that it is advantageous to use as small a flask as possible and to employ a still-head of as small capacity as is consistent with efficiency. A plain, wide still-head or one with spherical bulbs is the least satisfactory, but the "pear" still-head, owing to the diminished capacity of the bulbs and the increased efficiency, gives much better results. Of all forms, the "evaporator" still-head is the best, because the capacity is relatively small, and the amount of condensed liquid in it is smaller than in any other of equal efficiency, and because almost the whole of the liquid returns to the still at the end of the distillation.

With a liquid of low viscosity, like one of the paraffins, the quantity of liquid left in the still-head is almost inappreciable, and in other cases it may be reduced to a very small amount by disconnecting the apparatus while still hot from the condenser, shaking out any liquid remaining in the funnels, and tilting the tube from side to side to facilitate the flow of the residual liquid back to the still.\*

When the liquid left at the end of the distillation was *n*-hexane, hardly a trace was visible in the still-head after cooling, even when left

\* In a new form of "evaporator" still-head, which will be described later, the little funnels are done away with, and the tube merely requires to be tilted while still hot.

in position, whilst with benzene as the final liquid, the amount could certainly be reduced to 0.1 gram by taking down the still-head while hot, as described.

For these reasons, the "evaporator" still-head was used for all determinations, except when ethyl alcohol, benzene and water, ethyl alcohol and hexane, or ethyl alcohol and water were distilled together.

As an example of the estimation of loss by evaporation, we may cite the distillation of mixtures of methyl alcohol and benzene, one with benzene, the other with methyl alcohol in excess over the amount present in the mixture of constant boiling point.

In each case, the distillation was stopped when the middle point was reached, and the liquid left in the still after cooling was weighed.

The results obtained were as follows :

	Benzene in excess.	Alcohol in excess.
Weight of distillate .....	128.7	132.0
Weight of liquid in still .....	24.9	27.2
Total.....	153.6	159.2
Weight of mixture taken .....	154.2	160.1
Loss by evaporation and in still-head ...	0.6	0.9

When the benzene was in excess it is quite certain that the weight of it left in the still-head was not greater than 0.1 gram, and the loss by evaporation was therefore taken to be 0.5 gram, and in the calculation of composition this amount was added to the observed weight of distillate.

Allowing the same amount, 0.5 gram, for loss by evaporation in the second distillation, that would leave 0.4 gram as the weight of liquid—mostly methyl alcohol—in the still-head, an amount which appears quite reasonable, for this more viscous liquid did not flow back nearly so freely, and there was a visibly much larger amount left in the still-head.

When the "evaporator" still-head was employed, the correction applied for loss by evaporation was usually 0.4 or 0.3 gram. With the 18-column dephlegmator, which was used for the other distillations, the loss was certainly greater, but could not be accurately estimated.

## EXPERIMENTAL.

### *Methyl Alcohol and Water.*

Two determinations were made to test the value of the method, mixtures of known composition being distilled, in one of which the alcohol, in the other the water, was in large excess.

*Methyl alcohol in large excess.*

Boiling points: Methyl alcohol, 64·7°; water, 100·0°; middle point, 82·35°.

Mixture taken.	Weight below middle point.	Percentage composition of mixture.		
		Found.		Taken.
		Uncorrected.	Corrected.	
Alcohol 90·9 Water 24·4 <hr/> 115·3	Observed 90·5 Corrected 90·8	Alcohol 78·5 Water 21·5 <hr/> 100·0	78·7 21·3 <hr/> 100·0	78·8 21·2 <hr/> 100·0

*Water in large excess.*

Mixture taken.	Weight below middle point.	Percentage composition of mixture.		
		Found.		Taken.
		Uncorrected.	Corrected.	
Alcohol 39·7 Water 161·5 <hr/> 201·2	Observed 33·9 Corrected 34·2	Alcohol 16·9 Water 83·1 <hr/> 100·0	17·0 83·0 <hr/> 100·0	19·7 80·3 <hr/> 100·0

This second result is apparently unsatisfactory, but it is always difficult to separate the more volatile component of a mixture when present in relatively small amount, and, in such a case, a second distillation is usually necessary. The first distillation was therefore continued until the temperature reached 100°, and the whole of the distillate, weighing 66·8 grams, was then redistilled, and the double correction for loss by evaporation was applied. The weight below the middle point was now 38·9, corrected 39·5, giving the percentage composition:

	Uncorrected.	Corrected.	Taken.
Alcohol .....	19·3	19·6	19·7
Water .....	80·7	80·4	80·3
	<hr/> 100·0	<hr/> 100·0	<hr/> 100·0

It will thus be seen that, by repeating the distillation, the result was as satisfactory as that given by a single distillation when the alcohol was

in excess. Even without correcting for loss by evaporation, the agreement is fairly good, but it is much improved by introducing the correction.

*isoAmyl Alcohol and Benzene.*

Boiling points: benzene,  $80.2^{\circ}$ ; *isoamyl alcohol*,  $132.05^{\circ}$ ; middle point,  $106.1^{\circ}$ .

Mixture taken.	Weight below middle point.	Percentage composition of mixture.		
		Found.		Taken.
		Uncorrected.	Corrected.	
Alcohol 26.6 Benzene 85.7	Observed 85.55 Corrected 85.85	Alcohol 23.8 Benzene 76.2	23.6 76.4	23.7 76.3
112.3		100.0	100.0	100.0

The separation is here an easy one and the agreement is exceedingly good.

*Mixtures of Constant Boiling Point.*

The first two experiments serve to show that the quantity of a mixture of constant boiling point may be estimated by the distillation method in the same way as a pure substance. The methods of experiment and of calculation are similar in all respects.

For the sake of brevity, a mixture of constant boiling point of two components will be referred to in this paper as a "binary" mixture and a mixture of constant boiling point of three components as a "ternary" mixture.

*isoPropyl Alcohol and Water.*

Boiling points: binary mixture,  $80.37^{\circ}$ ; water,  $100.0^{\circ}$ ; middle point,  $90.2^{\circ}$ .

Mixture taken.	Weight below middle point.	Percentage composition of mixture.		
		Found.		Taken.
		Uncorrected.	Corrected.	
Binary } 57.7 mixture Water 20.1	Observed 57.3 Corrected 57.6	Binary } 73.65 mixture Water 26.35	74.05 25.95	74.15 25.85
77.8		100.00	100.00	100.00

The agreement in this case is perfectly satisfactory.

*tert. Butyl Alcohol and Water.*

Boiling points: binary mixture, 79·91°; water, 100·0°; middle point, 89·95°.

Mixture taken.	Weight below middle point.	Percentage composition of mixture.		
		Found.		Taken.
		Uncorrected.	Corrected.	
Binary mixture } 58·8 Water } 29·5 <hr/> 88·8	Observed 58·2 Corrected 58·5	Binary mixture } 65·9 Water } 34·1 <hr/> 100·0	66·25 33·75 <hr/> 100·00	66·6 33·4 <hr/> 100·0

Here the agreement is not quite so good, but may be regarded as fairly satisfactory.

In the following experiments, the composition of the mixtures of minimum boiling point was calculated from the results of the distillations.

*n-Propyl Alcohol and Water.*

For this distillation, a mixture of dry *n*-propyl alcohol with water was employed.

Boiling points: binary mixture, 87·72°; water, 100·0°; middle point, 93·85°.

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.		
		By distillation.		From specific gravity.
		Uncorrected.	Corrected.	
Alcohol 76·6 Water 50·0 <hr/> 126·6	Observed 106·4 Corrected 106·7	Alcohol 72·0 Water 28·0 <hr/> 100·0	71·8 28·2 <hr/> 100·0	71·69 28·31 <hr/> 100·0

The calculation is based on the following considerations. If the fractionation were complete, the original mixture would separate into (1) the binary mixture containing the whole of the alcohol, (2) the excess of water. The weight of the binary mixture is given by the corrected weight of distillate below the middle point, and thus the weight of alcohol in the binary mixture and that of the binary mixture itself are ascertained.



The statement may be made, generally, thus: The ratio of the weight of the component not in excess in the original mixture to the corrected weight of distillate is equal to the proportion of that component in the binary mixture.

Thus, in the actual distillation: Weight of alcohol = 76.6 grams; weight of binary mixture = corrected weight of distillate below middle point = 106.7 grams. Percentage of alcohol in binary mixture =  $\frac{76.6 \times 100}{106.7} = 71.8$ .

The determination of the composition of the binary mixture by means of the sp. gr. has already been referred to in the paper on the properties of mixtures of the lower alcohols with water.

It will be seen that the agreement is very satisfactory.

*isoAmyl Alcohol and Water.*

1. *Water in excess.*

Boiling points: binary mixture, 95.15°; water, 100.0°; middle point, 97.6°.

Mixture taken.	Weight below middle point.	Percentage composition of binary mixtures.	
		Uncorrected.	Corrected.
Alcohol 88.8 Water 69.5 <hr/> 108.3	Observed 76.4 Corrected 76.9*	Alcohol 50.8 Water 49.2 <hr/> 100.0	50.5 49.5 <hr/> 100.0

\* The correction introduced is slightly larger than usual on account of a minute loss of vapour during the distillation.

2. *Alcohol in excess.*

Boiling points: binary mixture, 95.15°; alcohol, 132.05°; middle point, 113.6°.

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.	
		Uncorrected.	Corrected.
Alcohol 68.8 Water 42.7 <hr/> 111.0	Observed 85.65 Corrected 85.95	Alcohol 50.1 Water 49.9 <hr/> 100.0	50.3 49.7 <hr/> 100.0

The agreement between the corrected values is very satisfactory.

*Methyl Alcohol and Benzene.*

These determinations have already been referred to in estimating the loss by evaporation ; full details are given below :

1. *Benzene in excess.*

Boiling points : binary mixture,  $58.34^{\circ}$  ; benzene,  $80.2^{\circ}$  ; middle point,  $69.25^{\circ}$ .

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.	
		Uncorrected.	Corrected.
Alcohol 51.2 Benzene 108.0 <hr/> 154.2	Observed 128.7 Corrected 129.2	Alcohol 39.8 Benzene 60.2 <hr/> 100.0	39.6 60.4 <hr/> 100.0

2. *Methyl alcohol in excess.*

Boiling points : binary mixture,  $58.34^{\circ}$  ; methyl alcohol,  $64.7^{\circ}$  ; middle point,  $61.5^{\circ}$ .

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.	
		Uncorrected.	Corrected.
Alcohol 79.9 Benzene 80.2 <hr/> 160.1	Observed 132.0 Corrected 132.5	Alcohol 39.2 Benzene 60.8 <hr/> 100.0	39.5 60.5 <hr/> 100.0

*Ethyl Alcohol and Benzene.*

Only one determination was made, the benzene being in excess, but the composition of the binary mixture was also ascertained by a determination of its sp. gr. as described in the previous paper (p. 741).

Boiling points : binary mixture,  $68.24^{\circ}$  ; benzene,  $80.2^{\circ}$  ; middle point,  $74.2^{\circ}$ .

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.		
		By distillation.		From specific gravity.
		Uncorrected.	Corrected.	
Alcohol 25.7 Benzene 78.5	Observed 78.9 Corrected 79.2	Alcohol 32.6 Benzene 67.4	32.45 67.55	32.36 67.64
104.2		100.0	100.00	100.00

*Ethyl Alcohol and Hexane.*

Two distillations were made, the mixture in each case containing excess of alcohol, but both the relative and actual quantities differed considerably. The 18-column dephlegmator was employed.

Boiling points: binary mixture, 58.68°; alcohol, 78.3°; middle point, 68.5°.

Mixture taken.	Weight below middle point.	Composition of binary mixture.	
		Uncorrected.	Corrected.
I. Alcohol 127.7 Hexane 128.4	Observed 161.1 Corrected 162.1	Alcohol 20.3 Hexane 79.7	20.3 79.2
256.1		100.0	100.0
II. Alcohol 72.5 Hexane 42.0	Observed 52.3 Corrected 53.4	Alcohol 20.5 Hexane 79.5	21.3 78.7
114.5		100.0	100.0

The agreement between the two corrected values is fairly satisfactory; the percentage of alcohol was taken to be 21.0.

*n-Propyl Alcohol and Benzene.*

In this case, two distillations were carried out, one of a mixture with benzene in excess, the other with alcohol in excess.

1. *Benzene in excess.*

Boiling points: binary mixture, 77.12°; benzene, 80.2°; middle point, 78.65°.

2. *Alcohol in excess.*

Boiling points: binary mixture,  $77.12^{\circ}$ ; alcohol,  $97.19^{\circ}$ ; middle point,  $87.15^{\circ}$ .

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.	
		Uncorrected.	Corrected.
<i>Benzene in excess.</i>			
Alcohol 26.95	Observed 158.8	Alcohol 17.0	16.95
Benzene 168.25	Corrected 159.2	Benzene 83.0	83.05
190.2		100.0	100.00
<i>Alcohol in excess.</i>			
Alcohol 40.2	Observed 96.0	Alcohol 16.7	16.95
Benzene 80.0	Corrected 96.3	Benzene 83.3	83.05
120.2		100.0	100.00

Here there is perfect agreement between the two corrected values.

*Composition of a Ternary Mixture.*

When a mixture of three liquids gives rise, on distillation, to the formation of a ternary mixture of minimum boiling point, the separation may, theoretically, take place in twelve different ways, and, in addition to these, if the original mixture had the same composition as the ternary mixture, its behaviour on distillation would be precisely that of a pure liquid.

Determinations were actually made with only one set of three liquids, and we may take this case, that of a mixture of ethyl alcohol, benzene, and water, as a typical one. For the sake of convenience, we will use the initial letters, A, B, and W, to represent the three components.

The possible cases are as follows:

	First fraction.	Second fraction.	Residue.
1.	A.B.W	A.W	W
2.	"	B.W	W
3.	"	A.W	A
4.	"	A.B	A

	First fraction.	Second fraction.	Residue.
5.	A.B.W.	B.W	B
6.	"	A.B	B
7.	"	—	A
8.	"	—	B
9.	"	—	W
10.	"	—	A.B
11.	"	—	A.W
12.	"	—	B.W
13.	"	—	—

The first six cases, and, on redistillation of the first fraction, the last, would be those commonly met with. For cases 7, 8, and 9, the relative quantities of two of the liquids would have to be precisely the same as in the ternary mixture, the third liquid being in excess. With regard to cases 10, 11, and 12, the composition of the original mixture would have to be exactly such as would be obtained by mixing together the pure ternary mixture with any one of the three pure binary mixtures, although, of course, any proportion of these two mixtures might be taken. Even if these conditions as regards cases 7 to 12 were fulfilled, it is doubtful whether, owing to imperfect separation, the results specified in the above table would be actually attained, but the matter has not been examined experimentally.

Of the first six cases, the third, when ethyl alcohol is employed, is unrealisable in practice, owing to the very small difference between the boiling points of the second fraction (A.W) and the residue (A).

Mixtures, however, tending to separate in the other five ways specified, were employed for the determination of the composition of the ternary mixture.

In order to calculate this, it is necessary to know, not only the composition of the original mixtures, but also that of the binary mixture forming the second fraction. The composition of each of the three binary mixtures is now known, and, for convenience of reference, the boiling points of all possible fractions, and the percentage composition of the binary mixtures, are given below :

	Boiling points.	Percentage composition.		
		A.	B.	W.
W. ....	100·0°	—	—	100
B. ....	80·2	—	100	—
A. ....	78·3	100	—	—
A.W. ....	78·15	95·57	—	4·43
B.W. ....	69·25	—	91·17	8·83
A.B. ....	68·24	32·36	67·64	—
A.B.W. ....	64·86			

In making up the original mixture, the materials employed were (1) 99.5 per cent. (by weight) alcohol, (2) pure benzene, (3) pure water, (4) the binary A.B. mixture.

## I.

Fractions : A.B.W. ; A.W. ; W. Middle points  $71.53^\circ$  and  $89.1^\circ$ .

Mixture taken.	Weights below middle points.		Composition of ternary mixture.	
	Observed.	Corrected.	Uncorrected.	Corrected.
A. 66.0 B. 74.2 W. 50.5 <hr/> 190.7	(1) 99.5 (2) 51.7	99.9 51.8	A. 16.7 B. 74.6 W. 8.7 <hr/> 100.0	16.5 74.3 9.2 <hr/> 100.0

In making the calculation, it is assumed, as before, that the corrected weights of the two distillates are equal to those of the ternary and binary mixtures respectively, which would be obtained if the separation were perfect.

That being so, in the above case, the weight of benzene in the ternary mixture is simply that of the benzene taken ; the weight of alcohol in the ternary mixture is the weight taken less that in the binary mixture, which can be calculated ; the weight of water is given by difference.

## II a and II b.

Two mixtures were distilled in this case.

Fractions : A.B.W. ; W.B. ; W. Middle points  $67.05^\circ$  and  $84.6^\circ$ .

Mixture taken.	Weights below middle points.		Composition of ternary mixture.	
	Observed.	Corrected.	Uncorrected.	Corrected.
IIa.				
A. 18.4 B. 120.0 W. 52.1 <hr/> 190.5	(1) 94.9 (2) 54.0	95.3 54.1	A. 19.4 B. 74.6 W. 6.0 <hr/> 100.0	19.3 74.2 6.5 <hr/> 100.0

Mixture taken.	Weights below middle point.		Composition of ternary mixture.	
	Observed.	Corrected.	Uncorrected.	Corrected.
	IIb.			
A. 18.5 B. 90.0 W. 54.3 <hr/> 162.8	(1) 95.3 (2) 20.7	95.7 20.8	A. 19.4 B. 74.6 W. 6.0 <hr/> 100.0	19.3 74.3 6.4 <hr/> 100.0

The agreement between the two results, notwithstanding the different relative quantities in the original mixture, is remarkable.

IV. Fractions: A.B.W. ; A.B. ; A. Middle points 66.55° and 73.3°

V. „ A.B.W. ; B.W ; B. „ 67.05 „ 74.7

VI. „ A.B.W. ; A.B. ; B. „ 66.55 „ 74.2

Mixture taken.	Weight below middle point.		Composition of ternary mixture.	
	Observed.	Corrected.	Uncorrected.	Corrected.
	IV.			
A. 75.0 B. 108.0 W. 7.5 <hr/> 190.5	(1). 100.6 (2). 47.5	101.0 47.6	A. 17.1 B. 75.4 W. 7.5 <hr/> 100.0	17.5 75.1 7.4 <hr/> 100.0
	V.			
A. 18.5 B. 160.1 W. 12.1 <hr/> 190.7	(1). 97.1 (2). 52.5	97.5 52.6	A. 19.1 B. 78.2 W. 7.7 <hr/> 100.0	19.0 78.4 7.6 <hr/> 100.0

Mixture taken.	Weight below middle point.		Composition of ternary mixture.	
	Observed.	Corrected.	Uncorrected.	Corrected.
	VI.			
A. 85.0	(1). 111.6	112.0	A. 19.0	18.9
B. 148.3	(2). 42.6	42.7	B. 74.2	74.3
W. 7.6			W. 6.8	6.8
190.9			100.0	100.0

The composition of the ternary mixture was directly determined, as described in the previous paper. The results of this determination and the mean of the results obtained by distillation, taking IIa and IIb as a single determination, are given below :

	Direct determination.	By distillation	
		uncorrected.	corrected.
Alcohol .....	18.5	18.3	18.2
Benzene.....	74.1	74.4	74.3
Water .....	7.4	7.3	7.5
	100.0	100.0	100.0

The agreement may be regarded as extremely satisfactory, although some of the individual values, especially those of alcohol and water in I, differ somewhat widely from the means. The explanation of the rather large errors in the first distillation is given on p. 767.

*Cases to which the Distillation Method is inapplicable.*

Of the numerous mixtures investigated, two only, *n*-hexane-benzene and ethyl alcohol-water, have given unsatisfactory results.

The relation of boiling point to molecular composition is very similar for both these mixtures; in both cases, the addition of moderate quantities of the less volatile component has very slight effect on the boiling point, but whereas with ethyl alcohol and water there is undoubtedly a definite mixture of minimum boiling point, the experimental results do not indicate with certainty whether benzene and *n*-hexane behave in this way, although it is extremely probable that such a mixture, boiling less than 0.05° lower than *n*-hexane, is actually formed.

The boiling points of various mixtures of benzene and hexane have



been determined by Jackson and Young (Trans., 1898, 73, 922), and a curve was drawn to represent the relation between the molecular composition and the boiling points. This curve is well reproduced by the formula  $t = 68.97^\circ - 0.0134m + 0.001366m^2 - 0.041360m^3 + 0.041248m^4$ , where  $t$  is the boiling point of the mixture and  $m$  the molecular percentage of benzene.

In the following table are given the molecular percentages of benzene and the boiling points, observed and calculated :

Molecular percentage of benzene.	Boiling points.			Molecular percentage of benzene.	Boiling points.		
	Observed	Calculated.	$\Delta$		Observed	Calculated.	$\Delta$
0	68.95°	68.97°	+0.02°	67.1	72.70°	72.64°	-0.06°
6.0	69.00	68.94	-0.06	69.4	78.01	72.97	-0.04
7.1	68.96	68.94	-0.02	79.6	74.67	74.71	+0.04
12.6	69.00	69.00	0	80.4	74.75	74.87	+0.12
18.6	69.14	69.12	-0.02	86.4	76.12	76.19	+0.07
29.3	69.47	69.50	+0.03	89.8	76.91	77.05	+0.14
33.8	69.72	69.72	0	90.9	77.20	77.85	+0.15
41.9	70.17	70.19	+0.02	92.7	77.75	77.85	+0.10
49.1	70.70	70.72	+0.02	94.5	78.49	78.88	-0.11
49.9	70.70	70.79	+0.09	95.7	78.80	78.74	-0.06
55.4	71.42	71.28	-0.14	100.0	80.20	80.17	-0.03

The formula appears to represent the results with sufficient accuracy to permit of its being employed for the calculation of the minimum boiling point. The calculated boiling points for mixtures containing 1, 2, . . . 10 per cent. are given below, and it will be seen that the minimum boiling point is 68.935°, or 0.035° below the calculated boiling point of *n*-hexane.

Molecular percentage of benzene.	Boiling point calculated.	Molecular percentage of benzene.	Boiling point calculated.
0	68.970°	6	68.936°
1	68.958	7	68.939
2	68.949	8	68.944
3	68.942	9	68.951
4	68.937	10	68.960
5	68.935		

It would appear from the above table that the mixture of minimum boiling point contains about 5 mols. per cent. of benzene, but the actual composition is somewhat uncertain owing to the flatness of the curve in this neighbourhood.

The estimation of the composition of a mixture by distillation is possible when the separation of the components, whether single substances or mixtures of constant boiling point, is practicable. In the case of ethyl alcohol and water, where the separation would be that of alcohol-water from water, we found that repeated fractional distillation with the most efficient still-head failed to give the pure mixture of constant boiling point. From a mixture of benzene and *n*-hexane it is impossible to separate either pure hexane or a mixture of constant composition. The following facts, bearing on this point, may be noticed about the benzene-hexane mixtures. (1) Benzene must be added until the mixture contains about 16 mols. per cent. before the boiling point rises  $0.1^{\circ}$  above that of hexane; (2) the boiling point of a mixture containing equal molecular proportions is  $70.8^{\circ}$ , or the rise of temperature is only  $1.85^{\circ}$  out of  $11.25^{\circ}$ , the difference between the boiling points of the pure components; (3) the mixture which has the boiling point  $74.6^{\circ}$ , midway between those of hexane and benzene, contains 79 molecules per cent. of benzene.

The ethyl alcohol-water curve, constructed from the data given by Noyes and Warfel (*J. Amer. Chem. Soc.*, 1901, 23, 463), is very similar in form to the *n*-hexane-benzene curve, but cannot be represented by so simple a formula. The following facts may be stated. (1) Water must be added until the mixture contains about 25 molecules per cent. before the boiling point rises  $0.1^{\circ}$  above that of pure alcohol; (2) the boiling point of a mixture containing equal molecular proportions is about  $79.8^{\circ}$ , or the rise of temperature is only  $1.5^{\circ}$  out of  $21.7^{\circ}$ , the difference between the boiling points of the pure components; (3) the mixture which has a boiling point  $89.15^{\circ}$ , midway between those of alcohol and water, contains about 93.5 mols. per cent. of water.

On distilling mixtures containing from 15 to 25 per cent. by weight of water through the 18-column dephlegmator and calculating the percentage of water in the mixture of constant boiling point in the usual way from the weight of distillate below the middle point, values from 7.6 to 8, instead of 4.43, per cent. were obtained, showing that too much water was carried down. Referring back to the calculation of the composition of the ternary ethyl alcohol-benzene-water mixture from the first distillation, if we take 7.8 as the percentage of water in the binary W.A. mixture, the calculated composition of the ternary mixture would become:

A .....	18.2
B .....	74.3
W .....	7.5
	<hr/>
	100.0

which agrees very well with that directly observed,

*General Conclusions.*

From the foregoing results, it will be seen that the distillation method, provided a very efficient still-head is used, may in the great majority of cases be safely employed for the determination of the composition of a mixture. But it must be borne in mind that from a mixture of two liquids it is almost always more difficult to separate the more volatile than the other component, and, therefore, if the original mixture contains a relatively very small amount of the more volatile component, a second distillation may be necessary, and a large quantity of the original mixture would be required in order to give a sufficient amount of distillate for a second operation. In such a case, the best plan is to continue the distillation the first time until the boiling point of the less volatile constituent is reached. No separation into fractions is necessary, but the whole of the distillate should be employed for the second operation, and the weight below the middle point then ascertained. A double correction for loss by evaporation must be introduced.

As regards the separation of three or more substances from a mixture, it may be pointed out that, as a general rule, the order as regards facility of separation is as follows: (1) the least volatile component, (2) the most volatile component, (3) the intermediate components.

It appears to be only when the curve representing the relation between boiling point and molecular composition is exceedingly flat at either end, as is the case for ethyl alcohol-water and for *n*-hexane-benzene when the more volatile component is in large excess, that the method is inapplicable.

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## LXXVII.—*The Vapour Pressures and Boiling Points of Mixed Liquids. Part I.*

By SYDNEY YOUNG, D.Sc., F.R.S.

It is well-known that when two non-miscible liquids are placed together in a vacuous space, the pressure exerted by the vapour is equal to the sum of the vapour pressures of the two substances when heated separately to the same temperature. If the two liquids are distilled together, the boiling point will be that temperature at which the sum of the two vapour pressures is equal to the barometric pressure. It will therefore be lower, frequently much lower, than the boiling point of either pure substance.

If the two liquids are miscible within limits, the vapour pressure will be lower than the sum of the vapour pressures of the components but will, in general, be higher, and the boiling point will be lower, than that of either pure component.

In the case of liquids miscible in all proportions, the vapour pressure and the boiling point may lie between those of the compounds or they may be higher or lower than those of either component; it is therefore not possible to make any general statement as to the relation of the vapour pressures or of the boiling points of such mixtures to those of their components.

The question, however, what should be regarded as the normal behaviour of two liquids miscible in all proportions has been discussed by several investigators. Guthrie (*Phil. Mag.*, 1884, [v], 18, 517) concluded that if we could find two liquids showing no contraction, expansion, or heat change on mixing, the vapour pressures should be expressed by a formula which reduces to

$$P = \frac{p \cdot P_A + (100 - p)P_B}{100}$$

where  $P$ ,  $P_A$ , and  $P_B$  are the vapour pressures of the mixture and of the two components  $A$  and  $B$  respectively at the same temperature, and  $p$  is the percentage by weight of the liquid  $A$ . In other words, the relation between the vapour pressure and the percentage composition by weight should be represented by a straight line.

Van der Waals (*Proc. Roy. Acad. Amsterdam*, 1900, 3, 170) considers that if the critical pressures of the two liquids are equal, and if the relation suggested by Galitzine and by Berthelot,  $a_{1,2} = \sqrt{a_1 a_2}$ , holds good ( $a_{1,2}$  represents the mutual attraction of the unlike molecules,  $a_1$  and  $a_2$  the attractions of the like molecules), the relation between vapour pressure and molecular composition should be represented by a straight line; or the equation already given should hold good if  $p$  is the molecular percentage of  $A$ .

Kohnstamm (*Inaug. Diss. Amsterdam*, 1901) has determined the vapour pressures of various mixtures of carbon tetrachloride and chlorobenzene, the critical pressures of which, 34180 mm. and 33910 mm., are nearly equal, and finds that the curvature, in this case is not very marked. At the temperature of experiment, the maximum deviation from the straight line amounted to a little over 6 mm. on a total observed pressure of 93.7 mm., or about 6.5 per cent.

It seems reasonable to suppose that the molecular attractions  $a_1$ ,  $a_2$ , and  $a_{1,2}$  should be most nearly equal, and the relation  $a_{1,2} = \sqrt{a_1 a_2}$  most likely to be true in the case of very closely related chemical compounds, such as the halogen derivatives of benzene, for which I have shown that many simple physical relations hold good. Thus the

critical pressures are equal or very nearly so; the ratio of the boiling points on the absolute scale is the same at all equal pressures, and consequently,  $dp/dt.T$  has the same value for both substances at all equal pressures; again, the ratio of the actual to the theoretical density at the critical pressure, and at other "corresponding," and therefore in this case equal, pressures, is the same for both.

Up to the present time, however, although the vapour pressures of many pairs of liquids have been determined, the substances are, so far as I know, with one exception less closely related than the halogen derivatives of benzene, and, probably with that exception, the relation between the vapour pressures and molecular composition is not represented by a straight line.

The exceptional case referred to is that of ethyl bromide and ethyl iodide, mixtures of which were investigated by Guthrie (*loc. cit.*).

The vapour pressures of ethyl chloride and ethyl bromide have been determined by Regnault up to about 5000 mm., and of ethyl iodide up to more than 500 mm., and within these limits, at any rate, the boiling points of any two of the liquids on the absolute scale bear a constant ratio to each other at all equal pressures, and it seems not improbable that, like the halogen derivatives of benzene, their critical pressures may be equal.

In the following table are given the vapour pressures at 16.7° observed by Guthrie, and those calculated from the formula  $P = \frac{p.P_1 + (100 - p)P_2}{100}$ , taking  $p$ , firstly, as percentage by weight, and secondly, as molecular percentage of ethyl bromide:

Percentages of ethyl bromide.		Vapour pressures.				
		Observed.	Calculated for $p$ = percentage.			
			By weight.	$\Delta$	Molecular.	$\Delta$
By weight.	Molecular.					
		mm.	mm.	mm.	mm.	mm.
100	100	452.2	452.2	0	452.2	0
90	92.79	428.2	423.3	- 4.9	431.4	+ 3.2
80	85.12	405.2	394.4	- 10.8	409.2	+ 4.0
70	76.94	380.4	365.5	- 14.9	385.5	+ 5.1
60	68.21	360.9	336.6	- 24.3	360.3	- 0.6
50	58.87	332.3	307.7	- 24.6	333.4	+ 1.1
40	48.81	306.4	278.8	- 27.6	304.2	- 2.2
30	38.00	276.4	249.9	- 26.5	273.0	- 3.4
20	26.34	246.9	221.0	- 25.9	239.3	- 7.3
10	13.71	214.8	192.1	- 22.7	202.8	- 12.0
0	0	163.2	163.2	0	163.2	0

There can be no question that the formula in which  $p$  = molecular percentage represents the results very much better than the other, and, with this meaning, although there is an individual deviation of 12 mm., the agreement between the calculated and observed pressures is fairly satisfactory, especially about the middle of the table, where the greatest differences would be expected.

Considering how difficult it is to obtain a mixture of known composition quite free from air, the deviations from the calculated values may perhaps be regarded as within the limits of experimental error. Some allowance may perhaps also be made for small fluctuations of temperature. As regards volume change on mixing, Guthrie's specific gravities are given only to two places of decimals, and therefore throw no light on the question whether expansion or contraction occurs.

### EXPERIMENTAL.

The experiments described in this paper were carried out in conjunction with Miss Fortey.

Fresh quantities of chlorobenzene and bromobenzene, obtained from Kahlbaum, were fractionated with a 12 bulb "pear" still-head, and the sp. gr. at  $0^{\circ}/4^{\circ}$  were determined. The agreement of the new results with those obtained by one of us in 1889 (*Trans.*, 55, 487) is satisfactory :

#### *Sp. gr. at $0^{\circ}/4^{\circ}$ .*

	New results.	Old results.
Chlorobenzene.....	1.12805	1.12786
Bromobenzene.....	1.52178	1.52182

A mixture of the two liquids in nearly molecular proportion, 11.2717 grams of chlorobenzene and 15.6960 grams of bromobenzene, was then made, and its sp. gr. at  $0^{\circ}/4^{\circ}$  was determined. It was noticed afterwards that the chlorobenzene from which a portion had been removed to make the mixture became slightly turbid when cooled to  $0^{\circ}$ , and therefore contained a trace of moisture, and it was possible that the mixture might also have been slightly moist. The sp. gr. of the moist chlorobenzene was therefore determined, and was found to be 1.12787 at  $0^{\circ}/4^{\circ}$ . The sp. gr. of the mixture was then calculated on the assumption that no change of volume occurs on mixing, taking the chlorobenzene in the mixture to be (a) dry, (b) moist :

#### *Sp. gr. of mixture at $0^{\circ}/4^{\circ}$ .*

Observed.....	1.32798	Calculated.....	a. 1.32804
			b. 1.32793

A second determination was made, again with nearly molecular quantities of the liquids :

	Weights taken.	Sp. gr. at 0°/4°.	
		Observed.	Calculated.
$C_6H_5Cl$ .....	11.4040	1.32860	1.32873
$C_6H_5Br$ .....	15.9930		

From these results, it appears that there is no perceptible change of volume on mixing the two liquids.

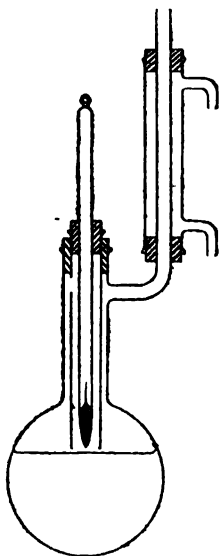
An experiment was next made to find whether any heat change occurs when the two liquids are mixed together in molecular proportion. The bromobenzene, 15.6 grams, was weighed in a small, round-bottomed flask, and the chlorobenzene, 11.2 grams, in a small beaker. The temperatures of the two liquids were determined, and the chlorobenzene was then poured into the flask, the mixture shaken, and the temperature again read. The results obtained are as follows :

	Chlorobenzene.	Bromobenzene.	Mixture.
Temp. ....	17.05°	17.00°	17.02°

There is therefore no perceptible evolution or absorption of heat on mixing the two liquids.

These results indicate that it would be impossible to find two liquids more likely to behave normally than chlorobenzene and bromobenzene.

Fig. 1.



*Vapour Pressures and Boiling Points of Mixtures of Chlorobenzene and Bromobenzene.*

Owing to the difficulty which is always experienced in obtaining a mixture of two liquids in known proportion entirely free from air and moisture, it was decided to employ the dynamical and not the statical method. The apparatus used is shown in Fig. 1. It consists of a bulb of about 155 c.c. capacity with a wide vertical tube, to which is sealed a narrow side tube cooled by water to act as a reflux condenser. The upper end of the side tube is connected with an exhaust and compression pump and a differential gauge. The wide vertical tube is provided with a well-fitting cork through which passes a rather narrower thin walled tube, which has a hole blown in it just below the

cork. This narrower tube is also fitted with a cork, through which passes the thermometer.

It is important that the volume of vapour should be as small as possible relatively to that of the liquid, and the bulb is therefore filled to about two-thirds of its capacity with liquid. The thin walled tube is pushed down until the bottom of it is about 3 mm. above the surface of the liquid when cold, and the bottom of the thermometer bulb is about level with the bottom of the thin walled tube.

This arrangement possesses the following advantages: (1) The liquid that returns from the reflux condenser cannot come near the thermometer, and the amount of liquid which condenses on the thermometer and on the inner walls of the thin walled tube is exceedingly small; on the other hand, with the large quantity of liquid which is present and the small flame that is required there is no fear of the vapour being superheated. (2) It is possible to take readings of the temperature both of the vapour and of the boiling liquid without altering the position of the thermometer, for when the burner is directly below the centre of the bulb, the liquid boils up into the thin walled tube well above the thermometer bulb, but when the burner is moved a little to one side, the surface of the liquid immediately below the thin walled tube remains undisturbed and the liquid does not come in contact with the thermometer bulb.

The apparatus was tested with pure chlorobenzene with the following results:

Pressure.	Temperature.		$\Delta$	Calculated from Biot's formula.
	Vapour.	Liquid.		
743·05	131·14°	131·54°	0·40	131·15°
728·20	130·37	130·77	0·40	130·41

The temperatures of the vapour agree well with those calculated from the constants for Biot's formula (Trans., 1889, 55, 487), and the agreement is even better if we calculate from the observed boiling point of the new sample of chlorobenzene. The liquid is evidently somewhat superheated.

The boiling points of three mixtures of chlorobenzene and bromobenzene were then determined through a range of about 100 mm. The temperatures of both vapour and liquid were read in each case, and it was found that for each mixture there was an almost constant difference between the two. The mean difference for each mixture (0·50°, 0·51°, and 0·57° respectively) was subtracted from the temperatures of the liquid, and the mean of the value so obtained and the temperature of the vapour was taken in each case as the true boiling point.

The experimental results are given in the table below:



*Boiling Points of Mixtures of Chlorobenzene and Bromobenzene.*

Molecular percentages of bromobenzene.

25·01.		50·00.		73·64	
Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
mm.		mm.		mm.	
685·0	132·86°	687·4	138·49°	685·4	144·14°
694·4	133·34	692·6	138·78	697·2	144·81
703·1	133·85	699·0	139·07	706·9	145·33
714·4	134·39	702·9	139·26	719·0	145·99
725·2	134·97	708·6	139·55	728·1	146·51
734·4	135·43	715·6	139·90	738·4	147·02
739·3	135·72	721·1	140·18	745·5	147·41
740·5	135·76	728·0	140·55	755·5	147·94
741·5	135·80	736·6	140·98	765·7	148·44
749·3	136·24	742·6	141·27	776·5	149·00
758·4	136·69	751·4	141·72	788·1	149·60
768·8	137·20	758·4	142·10	—	—
779·0	137·70	765·7	142·43	—	—
789·0	138·18	775·4	142·87	—	—

From these data, curves were constructed and the boiling points were read off at 700, 730, 760, and 790 mm. pressure.

Pressure.	Molecular percentage of bromobenzene.		
	25·01	50·00	73·64
mm.			
700	133·66°	139·10°	144·97°
730	135·22	140·67	146·59
760	136·75	142·16	148·16
790	138·22	143·60	149·67

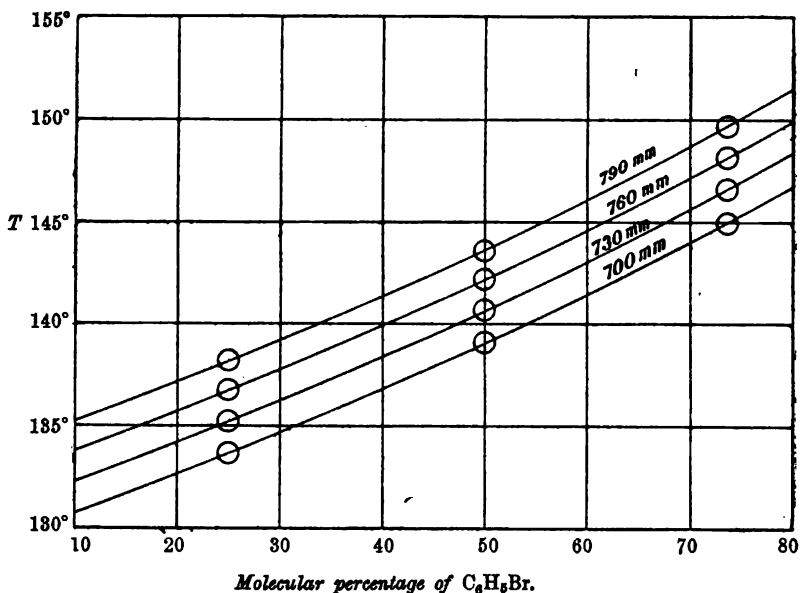
If, now, for each pressure we plot the temperatures against the molecular percentages of bromobenzene, including the boiling points of the pure substances ( $p=0$  and 100), the four isobars so obtained will be obviously curved, but the number of points is not sufficient to enable us to draw the curves accurately.

In order, however, to find whether the results are in agreement with the proposition that the isothermals, representing the relation between vapour pressure and molecular composition, are straight lines, we may proceed in either of two ways.

1. From the formula  $P = \frac{p.P_A + (100 - p)P_B}{100}$  we get  $p = \frac{100(P_B - P)}{P_B - P_A}$ ,

where  $p$  is the molecular percentage of bromobenzene and  $P_A$  and  $P_B$  are the vapour pressures of pure bromobenzene and chlorobenzene respectively at the boiling point of the mixture, and  $P$  is the pressure under which the mixture is boiling. We may then calculate from the formula the percentage of bromobenzene for the values 700, 730, 760, and 790 of  $P$  at a series of temperatures, and so obtain the theoretical isobars. It can then be seen whether the observed temperatures fall on them. For the vapour pressures of bromobenzene, from 130° to 156°, the

FIG. 2.



values given by Ramsay and Young (Trans., 1885, 47, 640) have been employed; the vapour pressures of chlorobenzene for the same temperatures have been calculated from the constants for Biot's formula (Young, *loc. cit.*), though for these nearly related substances, since the ratio of the boiling points on the absolute scale is a constant at all equal pressures, it would be sufficient to know the value of this ratio and the vapour pressure of one of the two substances.

The theoretical isobars are given in Fig. 2, and the experimental values are indicated by circles; it will be seen that the agreement is very good.

2. We may calculate the vapour pressures of the two pure liquids at

the boiling points of the mixtures, and then, from the equation

$$P = \frac{p \cdot P_A + (100 - p)P_B}{100},$$

we may calculate the theoretical values of  $P$ .

In the following table are given the vapour pressures of chlorobenzene and bromobenzene at the boiling points of the mixtures, and the values of  $F$  calculated by means of the above formula :

Molecular percentage of $C_6H_5Br$ .	$t$ .	Vapour pressures at $t^\circ$ .		P calc.	Observed pressure.	$\Delta$
		$C_6H_5Br$ .	$C_6H_5Cl$ .			
25.01	133.66°	414.6	795.05	699.9	700.0	-0.1
50.00	139.10	483.7	917.5	700.6	"	+0.6
73.64	144.97	568.05	1065.4	699.15	"	-0.85
			Mean...	699.9		-0.1
25.01	135.22	433.6	828.8	729.95	730.0	-0.05
50.00	140.67	505.2	955.35	730.3	"	+0.3
73.64	146.59	593.25	1109.3	729.3	"	-0.7
			Mean...	729.85		-0.15
25.01	136.75	452.85	862.95	760.4	760.0	+0.4
50.00	142.16	526.25	992.3	759.3	"	-0.7
73.64	148.16	618.4	1153.0	759.3	"	-0.7
			Mean...	759.7		-0.3
25.01	138.22	471.85	896.65	790.4	790.0	+0.4
50.00	143.60	547.35	1029.25	788.3	"	-1.7
73.64	149.67	643.55	1196.5	789.3	"	-0.7
			Mean...	789.3		-0.7

The differences between the pressures calculated from the formula and those under which the mixtures boiled are quite within the limits of experimental error ; the experimental results therefore prove that for the two liquids, chlorobenzene and bromobenzene, which are chemically so closely related, and which, in many ways, exhibit such simple physical relations, the vapour pressures of a mixture at any temperature are accurately expressed by the formula

$$P = \frac{p \cdot P_A + (100 - p)P_B}{100},$$

or, in other words, the relation between the vapour pressures and the molecular composition of mixtures at any temperature is represented graphically by a straight line.

It is proposed to extend the investigation to mixtures of other liquids.

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LXXVIII.—*Correction of the Boiling Points of Liquids from Observed to Normal Pressure.*

By SYDNEY YOUNG, D.Sc., F.R.S.

IN papers published jointly with Dr. Ramsay (*Brit. Assoc. Rep.*, 1885, 928; *Phil. Mag.*, 1885, [v], 20, 515), it was pointed out that (1) the values of  $dp/dt \cdot T$  (where  $dp/dt$  is the rate of increase of vapour pressure per unit rise of temperature, and  $T$  is the boiling point on the absolute scale) are approximately the same for different substances when compared at the same pressure, but that (2) the differences are real and are not due to errors of experiment, for they preserve the same relative value whatever the pressure at which the comparison is made, at any rate within the limits of the actual experiments. It was further pointed out that for two closely-related substances, the boiling points on the absolute scale bear a constant ratio to each other at all pressures, and that for other substances (*Phil. Mag.*, 1886, [v], 21, 33) the relation between the boiling points may be expressed by an equation which can be written thus:

$$\frac{T_A'}{T_B'} = \frac{T_A}{T_B} + C(T_B' - T_B),$$

where  $T_A'$  and  $T_B'$  are the boiling points of the two substances on the absolute scale at a pressure,  $p'$ ,  $T_A$  and  $T_B$  the boiling points at a pressure,  $p$ , and  $c$  is a very small constant.

In the light of these generalisations, Crafts (*Ber.*, 1887, 20, 709) devised a convenient method for the correction of the boiling points of substances from observed to normal pressure.

Crafts gives the boiling points (absolute temperatures), the values of  $\Delta t/\Delta p$  between 720 and 770 mm. pressure, and the quotients  $\frac{\Delta t}{\Delta p} \cdot \frac{1}{T} = H$  for 25 substances, and points out that when the boiling point of any liquid is to be corrected, the constant,  $H$ , for that compound in the table most closely related to it is to be taken and is to be multiplied by the approximate absolute boiling point of the substance under examination, in order to find the value of  $\Delta t/\Delta p$  for a barometric variation of the 50 mm. between 720 and 770 mm.

Nernst (*Theoretische Chemie*, 1893, p. 55) reproduces this table, but divides the constants,  $H$ , by 50, so as to give the mean variation of temperature per mm. change of pressure between the same limits.

There are a few misprints in Crafts' table which reappear in the modified table given by Nernst, and since 1887 the vapour pressures of a considerable number of additional compounds have been accurately determined; it may therefore be useful to give a revised and enlarged table for reference.

Instead of calculating the mean value of the constant for a range of pressure between 720 and 770 mm., I have thought it better to give the actual value of  $\frac{dt}{dp} \cdot \frac{1}{T} = C$  at 760 mm., and therefore the constants in this paper differ slightly from those in Nernst's table; in most cases, the new values are lower by 2 in the last place, and this may be taken as the average difference between the value of  $C$  at 760 mm. and the mean value between 720 and 770 mm.

In calculating the value of  $dp/dt$  at the boiling point, Biot's formula,  $\log p = a + ba^t + c\beta^t$ , was employed when the constants for this formula had already been ascertained; in other cases, for which the vapour pressures have been determined through a sufficient range of temperature, constants for the simpler formula,  $\log p = a + ba^t$ , were calculated from the vapour pressures at three temperatures 20°, 30°, or 40° apart, the middle temperature being near the boiling point under normal pressure. This method was adopted, for example, in the case of the 29 esters of the methyl formate series for which accurate data are available.

For the elementary gases, and for carbon monoxide and methane, the vapour pressure data are not sufficient for this method to be employed, and the formula,  $\frac{T'_A}{T'_B} = \frac{T^u}{T_B} + c(T'_B - T_B)$ , was made use of, benzene being taken as the standard substance. The constant,  $c$ , was first calculated from the boiling point and critical temperature of the gas and the boiling point of benzene under normal pressure and at a pressure equal to the critical pressure of the gas, the assumption being made that Biot's formula might be employed for benzene for some little distance above its actual critical point. It is probable that the boiling points and critical constants of the gases are less accurately known than the vapour pressures of the majority of substances included in the tables that follow, and as the method of calculation of  $dp/dt$  is also less direct, the values of  $C$  are probably less accurate. The constants determined in this way are marked with an asterisk.

$$\text{Values of } C = \frac{dt}{dp} \cdot \frac{1}{T} \text{ at 760 mm.}$$

Name of substance.	Boiling point (abs. temp.).	$dp/dt$	$C$ .	Observer.
Oxygen .....	90.3°	75.9	0.000146	Olazewski.
Nitrogen .....	77.5	89.0	0.000145	Baly.
Argon .....	86.9	83.2	0.000138	Ramsay and Travers.
Krypton .....	121.3	61.8	0.000133	" "
Xenon .....	163.9	45.9	0.000133	" "
Chlorine .....	239.4	33.2	0.000126	Knietsch.
Bromine .....	331.75	25.2	0.000120	Ramsay and Young
Iodine .....	453.3	18.75	0.000118	" "
Mercury .....	629.8	13.4	0.000118	Young.
Sulphur.....	721.4	12.2	0.000114	Regnault.
Carbon monoxide... *	83.0	81.3	0.000148	Olazewski.
Sulphur dioxide .....	262.9	33.7	0.000113	Regnault.
Ammonia .....	240.1	37.7	0.000110	"
Carbon disulphide ...	319.25	24.7	0.000127	"
Boron trichloride.....	291.25	26.8	0.000128	"
Phosphorus trichloride .....	346.85	23.45	0.000123	"
Silicon tetrachloride .....	329.9	24.0	0.000126	"
Stannic chloride .....	337.1	21.4	0.000121	"
Methyl chloride .....	249.35	31.9	0.000126	"
Chloroform .....	333.2	25.2	0.000119	"
Carbon tetrachloride .....	349.75	23.25	0.000123	Young.
Methane .....	109.0	68.2	0.000135	Olazewski.
n-Pentane .....	309.3	25.8	0.000125	Young.
n-Hexane .....	341.95	23.9	0.000122	"
n-Heptane .....	371.4	22.3	0.000121	"
n-Octane .....	398.8	21.1	0.000119	"
isoPentane .....	300.95	26.2	0.000127	"
Diisopropyl .....	331.1	24.3	0.000124	Young and Fortey.
Diisobutyl .....	382.1	20.9	0.000125	" "
cycloHexane .....	353.9	22.7	0.000124	" "
Benzene .....	353.2	23.3	0.000122	Young.
Toluene.....	383.7	21.8	0.000120	Young and Fortey.
Naphthalene .....	491	17.1	0.000119	Crafts.
Anthracene .....	616	15.0	0.000108	"
m-Xylene .....	412	21.1	0.000115	"
Diphenylmethane ...	538	15.1	0.000123	"
Triphenylmethane ...	626	14.8	0.000108	"
Fluorobenzene .....	358.2	23.3	0.000120	Young.
Chlorobenzene .....	405.0	20.5	0.000120	"
Bromobenzene .....	429.0	19.3	0.000120	"
Iodobenzene.....	461.45	18.0	0.000120	"
Bromonaphthalene ...	553.45	15.75	0.000115	Ramsay and Young.
Ethylene dibromide .....	405	20.8	0.000119	Crafts.
Methyl ether .....	249.4	32.0	0.000125	Regnault.
Ethyl ether .....	307.6	26.9	0.000121	Ramsay and Young.
Acetone.....	330	26.4	0.000115	Crafts.

Values of  $C = \frac{dt}{dp} \cdot \frac{1}{T}$  at 760 mm. (continued).

Name of substance.	Boiling point (abs. temp.).	$dp/dt$ .	$C$ .	Observer.
Benzophenone .....	578.8°	15.8	0.000109	Crafts.
Dibenzylketone .....	603.55	15.2	0.000109	Young.
Anthraquinone .....	650	13.6	0.000113	Crafts.
Aniline .....	457.4	19.6	0.000112	Ramsay and Young.
Quinoline .....	510.5	17.0	0.000115	Young.
Methyl formate .....	304.9	23.8	0.000114	Young and Thomas.
Ethyl formate .....	327.3	26.6	0.000115	" "
Methyl acetate .....	330.1	26.8	0.000113	" "
Propyl formate .....	353.9	24.5	0.000115	" "
Ethyl acetate .....	350.15	25.1	0.000114	" "
Methyl propionate ...	352.7	24.9	0.000114	" "
isoButyl formate.....	370.85	23.45	0.000115	Schumann.
Propyl acetate.....	374.55	23.5	0.000114	Young and Thomas.
Ethyl propionate.....	372.0	23.7	0.000113	" "
Methyl butyrate .....	375.75	23.3	0.000114	" "
Methyl isobutyrate...	365.3	23.8	0.000115	" "
Amyl formate .....	396.25	21.8	0.000115	Schumann.
isoButyl acetate .....	389.2	22.5	0.000114	" "
Propyl propionate ...	395.15	22.3	0.000114	" "
Ethyl butyrate .....	392.9	22.3	0.000114	" "
Ethyl isobutyrate ...	383.1	22.5	0.000113	" "
Methyl valerate .....	389.7	22.4	0.000114	" "
isoButyl propionate	409.8	21.4	0.000114	" "
Propyl butyrate .....	415.7	20.9	0.000115	" "
Propyl isobutyrate ...	406.9	21.8	0.000113	" "
isoPropyl isobutyrate	393.75	22.0	0.000115	Young and Fortey.
Ethyl valerate .....	407.3	21.4	0.000115	Schumann.
Amyl propionate.....	433.2	20.4	0.000113	" "
isoButyl butyrate ...	429.9	20.5	0.000113	" "
isoButyl isobutyrate	419.6	20.6	0.000113	" "
Propyl valerate .....	428.9	20.5	0.000114	" "
Amyl butyrate.....	451.6	19.5	0.000113	" "
Amyl isobutyrate ...	441.8	19.6	0.000115	" "
isoButyl valerate.....	441.7	19.9	0.000114	" "
Methyl alcohol.....	337.9	29.6	0.000100	Ramsay and Young.
Ethyl alcohol .....	351.3	30.35	0.000094	" "
Propyl alcohol.....	370.4	28.8	0.000094	" "
Amyl alcohol .....	403	25.3	0.000098	Crafts.
Phenol .....	456	20.5	0.000107	" "
Acetic acid .....	391.5	23.9	0.000107	Young.
Phthalic anhydride...	559	16.0	0.000112	Crafts.
Sulphobenzide .....	652	15.2	0.000101	" "
Water .....	373.0	27.2	0.000099	Regnault.

It will be seen that the values of  $C$  ( $\times 10^6$ ) vary from about 145 in the case of oxygen, nitrogen, and carbon monoxide to 99 for water and 94 or ethyl and propyl alcohols.

The following relations are clearly observable :

1. In most groups of similar substances the greater the molecular complexity the lower is the constant. This is well seen in the case of the normal paraffins ; of benzene, naphthalene, and anthracene ; of methyl and ethyl ether, and of acetone and benzophenone or dibenzyl ketone.

2. Rise of molecular weight without increased complexity either causes a similar change or has no influence ; thus, for the halogens  $C$  diminishes from chlorine to iodine ; but, on the other hand, it has the same value for the four halogen derivatives of benzene.

3. Comparing isomeric substances, it is seen that  $C$  is almost always lower for normal than for *iso*-compounds, and lower for these than for compounds that contain two *iso*-groups.

4. By replacement of hydrogen by a halogen, the constant is lowered ; thus benzene, 122, chlorobenzene 120 ; naphthalene 119, bromonaphthalene 115 ; ethane, above 125, ethylene dibromide, 119.

5. When there is association of molecules in the liquid state, the value is low ; this is the case with water, the alcohols, phenol, and acetic acid, all of which contain a hydroxyl group.

6. In the case of organic hydroxyl compounds, the influence of the hydroxyl group diminishes as the complexity of the organic radicle increases, and thus the depression of the constant diminishes, but, on the other hand, the constant tends to fall as the complexity of the molecule increases. There are thus two opposing influences, and in the group of alcohols the constant shows considerable irregularity.

In the case of the esters, there is evidence of some molecular association in the liquid state and at the critical point, and we find similar opposing influences, with the result that the variation in the constant is very small ; indeed, for the whole 29 esters the extreme values are 113 and 116. Still, if we confine our attention to the higher esters containing, say, 5 or more carbon atoms, (1) the influence of molecular complexity, and (2) of constitution, is, with few exceptions, to be observed, and in the table on p. 782 the results are summarised to bring out this point :

In order to correct a boiling point from observed to normal pressure,  $\Delta t$  is to be added, where

$$\Delta t = (760 - p)(273 + t).C.$$

The constant  $C$  is to be ascertained from the preceding tables, taking account, if necessary, of the relations (1) to (6) ;  $p$  is the observed pressure and  $t$  is the boiling point as observed or, better, roughly corrected.

In a series of papers (*Phil. Mag.*, 1892, [v], 34, 503 ; *Trans.*, 1893, 63, 1254 ; *Phil. Mag.*, 1894, [v], 37, 1 ; *ibid.*, 1900, [v], 50, 291), I



Formula of ester.	Normal.		One iso-group.		Two iso-groups.	
	C.	Mean.	C.	Mean.	C.	Mean.
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	0·0001139	0·0001139	—	—	—	—
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	0·0001149	0·0001140	—	—	—	—
	0·0001130		—	—	—	—
	0·0001151		—	—	—	—
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	0·0001138	0·0001142	—	—	—	—
	0·0001136		—	—	—	—
	0·0001142		—	—	—	—
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	0·0001134	0·0001137	0·0001150	0·0001150	—	—
	0·0001136		0·0001150		—	—
	0·0001136		0·0001155		—	—
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	0·0001137	0·0001139	0·0001139	0·0001149	—	—
	0·0001141		0·0001153		—	—
			0·0001143		—	—
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	0·0001148	0·0001148	0·0001140	0·0001138	0·0001155	0·0001155
			0·0001147			
			0·0001127			
C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	—	—	0·0001129	0·0001133	0·0001156	0·0001156
			0·0001135			
			0·0001136			
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	—	—	0·0001134	0·0001134	0·0001152	0·0001145
					0·0001138	
Mean...	0·0001140		0·0001142		0·0001150	

have shown that, excluding compounds which contain a hydroxyl group, the ratio,  $\frac{D_c}{D'_c}$ , of the actual to the theoretical density for a perfect gas at the critical point is approximately constant, the mean value being about 3·76, but that the deviations are real ones and are related to the molecular weight and constitution of the substances.

I have also shown that Cailletet and Mathias' law of the "diameter" is not in most cases absolutely true, although very nearly so, and that the relation of the mean density to the temperature should be expressed by the formula  $D_t = D_0 + at + \beta t^2$ , where  $\alpha$  is always negative, and  $\beta$  changes from a very small positive value, through zero, to a very small negative value as the ratio  $\frac{D_c}{D'_c}$  increases.

Again taking the approximate formula  $D_t = D_0 + at$ , originally given by Cailletet and Mathias, it has been proved independently by Mathias and myself that, if the generalisations of Van der Waals were strictly true,  $\frac{\alpha T_c}{D_c}$  should be a constant for all substances; but I have shown that there are real though not large deviations in this case also, the value of  $\frac{\alpha T_c}{D_c}$  rising in general as  $\frac{D_c}{D'_c}$  increases.

It is of interest to observe that, as a rule,  $C \left( = \frac{d \, t_1}{dp \, T} \right)$  at normal pressure diminishes as  $\frac{D_c}{D_c'}$  rises.

So far, then, as the 26 substances which I have myself examined are concerned, there is clearly a connection between the four constants  $\frac{D_c}{D_c'}$ ,  $\beta$ ,  $\frac{\alpha T_c}{D_c}$ , and  $C$ .

The critical densities of the gaseous elements are not known with sufficient precision to allow of any very definite statement being made regarding the value of  $\frac{D_c}{D_c'}$ , but it is interesting to note that D. Berthelot points out that for carbon dioxide this constant is lower (3.6) than for any of the substances I have investigated, whilst for oxygen and nitrogen it appears to be about 3.5.

The constant  $C \, (\times 10^6)$  for the two last named gases is about 145, and if a diagram is constructed to show the relation between  $C$  and  $\frac{D_c}{D_c'}$  and these values,  $C = 145$  and  $\frac{D_c}{D_c'} = 3.5$  are mapped with the others, including also those of ethyl and propyl alcohols, the connection between  $C$  and  $\frac{D_c}{D_c'}$  becomes quite evident, the former falling as the latter rises. Methyl alcohol and acetic acid have low, but not proportionately low, values of the constant  $C$ .

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## LXXIX.—*Vapour Pressures and Specific Volumes of isoPropyl isoButyrate.*

By SYDNEY YOUNG, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

IN the preparation of diisopropyl by the electrolysis of potassium isobutyrate, it was found that the yield of hydrocarbon was exceedingly poor, but that, on the other hand, a considerable quantity of isopropyl isobutyrate was formed.

The isobutyric acid was carefully fractionated before its potassium salt was electrolysed, and the isopropyl isobutyrate was therefore easily purified; after three fractionations, it boiled quite constantly at  $120.75^\circ$  under normal pressure.

A second specimen of the ester was prepared by saturating a mix-

ture of pure *isobutyric* acid and *isopropyl* alcohol with hydrogen chloride in the usual manner. The boiling point was found to be identical with that of the ester obtained by the electrolytic method.

The sp. gr. of both specimens were determined at 0°, and that of the second specimen at 21·35°, with the modified Sprengel tube. The weighings were reduced to a vacuum. As the ester, when even slightly moist, rapidly acquired an acid reaction owing to hydrolysis, it was found necessary to remove the free acid from time to time by means of sodium hydroxide, and the free alcohol and water by means of phosphoric oxide. The sp. gr. and boiling point were determined after each of these operations.

*Specific gravities.*

Ester obtained by electrolysis.

At 0° 0·86867

Ester obtained from acid and alcohol.

At 0° (1) 0·86874

(2) 0·86874

At 21·35° 0·84708

Mixture at 0° (1) 0·86874

(2) 0·86873

Mean sp. gr. at 0° = 0·86872

*Boiling points.*

Ester obtained by electrolysis.  
Temperature

Pressure.	Temperature	
	obs.	corr. to 760 mm.
753·0 mm.	120·45°	120·77°
—	—	—
—	—	—

Ester obtained from acid and alcohol.  
Temperature

Pressure.	Temperature	
	obs.	corr. to 760 mm.
756·15 mm.	120·6°	120·77°
763·0 „	120·9	120·72
755·4 „	120·55	120·76

Mean 120 75

Mixture of the esters.

Pressure.	Temperature.	
	obs.	corr. to 760 mm.
761·0 mm.	120·80°	120·75°
771·3 „	121·32	120·81
763·9 „	120·9	120·72
738·8 „	119·77	120·73
747·6 „	120·27	120·83

Mean 120·77

General mean = 120·76°.

The value of  $dp/dt$ , calculated from Biot's formula, is 22·0 mm. per degree.

*Vapour Pressures at Low Temperatures.*

For pressures up to 170 mm., the method of Ramsay and Young was used; from 150 mm. to the atmospheric pressure, a modified distillation bulb with a reflux condenser was employed.

Pressure.	Tem- perature.	Pressure.	Tem- perature.	Pressure.	Tem- perature.	Pressure.	Tem- perature.
5.8	7.85°	14.3	23.5°	36.7	40.7°	91.05	60.7°
6.55	10.35	16.55	25.7	41.8	43.55	102.65	63.6
7.85	12.95	19.05	28.3	47.65	46.3	115.25	66.15
8.85	14.95	21.55	30.4	54.85	49.4	129.75	69.0
10.0	17.1	24.8	33.2	62.25	52.0	145.0	71.85
11.25	19.2	28.1	35.55	70.6	54.8	163.0	74.85
12.8	21.4	32.15	38.35	80.1	57.65	172.0	76.1
148.4	72.1	246.0	85.55	411.3	100.4	645.9	115.2
158.65	78.9	272.7	88.28	449.9	103.3	703.9	118.15
175.4	76.6	305.7	91.75	493.1	108.2	770.7	121.3
195.35	79.25	339.0	94.8	541.4	109.2	—	—
220.3	82.5	378.6	97.45	590.8	112.1	—	—

*Vapour Pressures at High Temperatures.*

The vapour pressures at high temperatures were determined with the pressure apparatus employed in previous researches. It would have been of interest, if possible, to ascertain the critical constants of isopropyl isobutyrate, on account of the presence of two *iso*-groups in the molecule, but, unfortunately, it was found that the ester began to decompose at about 230°, and that at 260° the decomposition was so rapid that it was quite impossible to obtain trustworthy results. The data above 230° are therefore not given, as they would only be misleading.

The observed pressures from 130° to 230° (the mean of four readings in each case), together with those read from the curve constructed from the observations at low temperatures, are given in the following table:

Vapour pressures:

Temperature.	Dynamical method from curve.	Temperature.	Statical method.
10°	6.55 mm.	130°	994 mm.
20	11.95 „	140	1290 „
30	20.9 „	150	1649 „
40	35.05 „	160	2096 „
50	56.9 „	170	2612 „

Temperature.	Dynamical method from curve.	Temperature.	Statistical method.
60°	89.0 mm.	180°	3216 mm.
70	136.0 „	190	3916 „
80	201.1 „	200	4742 „
90	289.4 „	210	5700 „
100	406.0 „	220	6785 „
110	553.4 „	230	8058 „
120	743.9 „		

*Volumes of a Gram of Liquid.*

These were determined in the pressure apparatus. At 220° and 230°, they were calculated from observations of the volume of vapour and the total volume of liquid or vapour (Trans., 1893, 63, 1200); the remaining volumes were read directly :

*Volumes of a Gram and Molecular Volumes of Liquid.*

Tem- perature.	Volumes of a gram in c.c.		Mole- cular volume in c.c.	Tem- perature.	Volumes of a gram in c.c.		Mole- cular volume in c.c.
	Observed.	From curve.			Observed.	From curve.	
0°	1.1511	1.1511	149.31	120°	1.3540	1.3539	175.62
10	—	1.1646	151.06	130	1.3769	1.3767	178.57
20	—	1.1788	152.90	140	1.4010	1.4005	181.66
30	1.1939	1.1934	154.79	150	1.4256	1.4257	184.93
40	1.2092	1.2085	156.75	160	1.4521	1.4528	188.44
50	1.2240	1.2243	158.80	170	1.4814	1.4818	192.14
60	1.2411	1.2405	160.91	180	1.5125	1.5128	196.22
70	1.2575	1.2573	163.08	190	1.5460	1.5462	200.56
80	1.2746	1.2749	165.37	200	1.5841	1.5845	205.52
90	1.2923	1.2934	167.76	210	1.6270	1.6273	211.08
100	1.3128	1.3126	170.26	220	1.6823	1.6765	217.46
110	1.3325	1.3328	172.88	230	1.7327	1.7331	224.80

The volume of a gram of saturated vapour was only determined satisfactorily at 230°. The result obtained was as follows :

Volume of a gram .....	21.05
Molecular volume .....	224.75

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LXXX.—*Influence of the Methyl Group on Ring Formation.*

By A. W. GILBODY and C. H. G. SPRANKLING.

THIS research was undertaken with the twofold object of studying the antipyretic effects obtained by successively introducing methyl groups into some substance already possessing the property of producing such effects, and of ascertaining what influence these methyl groups would have on the stability of the mother substance.

Pyrantin (*p*-ethoxyphenylsuccinimide) was chosen as a basis because it had already been shown to be an excellent antipyretic (Piutti, *Ber.*, 1896, 29, 85), and by using methylsuccinic acids or their anhydrides instead of succinic acid itself for the preparation, methyl groups could readily be introduced into the imide ring.

The first study was unsuccessful because the pyrantin derivatives were almost insoluble in weak (0.75 per cent.) sodium chloride solution at 30°, the solubilities ranging from 1:713 for pyrantin to 1:1272 for trimethylpyrantin.

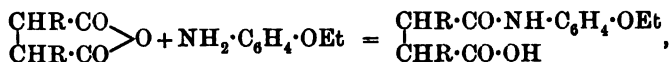
As another source of antipyretic substances, it was then attempted to prepare the sodium salts of the intermediate methyl-substituted *p*-ethoxyphenylsuccinamic acids containing an open chain, as for example, *cis-s*-dimethyl-*p*-ethoxyphenylsuccinamic acid (*cis-s*-dimethyl-*p*-ethoxysuccinanic acid), but it was found that these sodium salts are unstable in aqueous solution when several methyl groups are present, owing to the great tendency to ring formation and consequently the study of the antipyretic action of the methyl group was abandoned.

The second object of the research was more successful, as the authors were able to ascertain the stability constants of the methylpyrantins which they had prepared according to the method devised by Miolati and his colleagues for the alkyl-, phenyl-, tolyl-, and xylyl-succinimides, where the radicle mentioned was substituted for the hydrogen atom attached to the nitrogen of the succinimide ring (compare Miolati and Longo, *Atti R. Accad. Lincei*, 1894, [v], 3, 515; 1895, [v], 4, 351; Miolati and Lotti, 1896, [v], 6, 88). The results of the experiments were then calculated from the formula used by Hantzsch and Miolati for the measurements of the stability of the oxazolone ring,  $C_6H_4 \begin{smallmatrix} < CR:N \\ & CO \cdot O \end{smallmatrix}$

namely,  $\frac{1}{T} \cdot \frac{x}{A-x} = Ac$  (*Zeit. physikal. Chem.*, 1893, 11, 748).

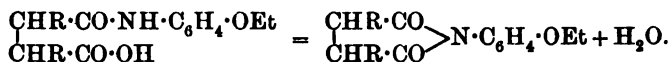
The reactions by which these substituted pyrantins were prepared took place in two stages, the open chain succinamic acid being first

prepared by the action of *p*-phenetidine upon the methylsuccinic anhydride, using benzene or toluene as the solvent:

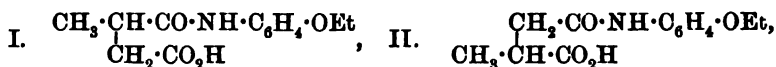


where R = a methyl group.

The substituted succinamic acid thus obtained was then heated alone above the melting point, when water was readily split off according to the equation:



Theory requires that some of the substituted succinamic acids should exist in two isomeric forms, as, for example, methyl-*p*-ethoxyphenylsuccinamic acid (methyl-*p*-ethoxysuccinamic acid),



but in the authors' experiments only one acid has been obtained, and they are unaware that any such isomerides have been prepared even in the case of the corresponding methylsuccinamic acids.

Pyrantin and *cis*-dimethylpyrantin can only exist in one form, but the other methylpyrantins which have been prepared, namely, methyl-, *trans*-(*l*)-dimethyl-, *as*-dimethyl-, trimethyl-, or *α*-isopropyl-pyranthin, should exist in two forms.

The authors have, however, been unable to determine experimentally which of the two possible formulæ is correct in the case of the methyl-*p*-ethoxyphenylsuccinamic acid obtained, but as Blaise (*Compt. rend.*, 1898, 126, 753) states that a tertiary carboxyl radicle is much more difficult to esterify than a primary one, it has been decided to adopt the formula in which the primary carboxyl is united with the amide group of the aromatic portion of the formula, and the secondary or tertiary group is free; thus formula II is taken as being correct for methyl-*p*-ethoxyphenylsuccinamic acid in the absence of evidence to the contrary.

The pyrantins were all obtained in a pure crystalline condition by removing any trace of colouring matter with a little glacial acetic acid and then crystallising from alcohol.

The modification in the method of measuring the stability constant consisted in using a pure alcoholic solution of the alkylpyrantin, on account of its insolubility in water, but aqueous standard solutions of caustic soda and hydrochloric acid were retained.

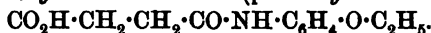
The values obtained for the pyrantins were then converted into those for the corresponding methylphenylsuccinimides in aqueous solution,

the detailed results, together with the conclusions deduced, being given after the experimental portion of the paper.

### EXPERIMENTAL.

#### I. *Preparation and Properties of the Succinamic Acids.*

##### *p*-Ethoxyphenylsuccinamic Acid (*p*-Ethoxysuccinamic Acid),



Slightly more than 1 mol. (15 grams) of *p*-phenetidine was added to 1 mol. (10 grams) of finely powdered succinic anhydride dissolved in toluene by digestion on the water-bath with a large volume of the solvent until solution was complete. After standing, much heat was developed and in a short time crystals separated which were filtered off, dried on a porous plate, and recrystallised from water, or better still from dilute alcohol.

The acid separated from alcohol in colourless, rectangular leaflets of pearly appearance which melted at 166—167°. After two or three recrystallisations, the melting point had not altered. On analysis:

0.2494 gave 0.5545  $\text{CO}_2$  and 0.1458  $\text{H}_2\text{O}$ . C = 60.66; H = 6.50.

0.2416 „ 12.4 c.c. moist nitrogen at 13° and 756 mm. N = 6.03.

$\text{C}_{12}\text{H}_{15}\text{O}_4\text{N}$  requires C = 60.76; H = 6.32; N = 5.90 per cent.

*p*-Ethoxyphenylsuccinamic acid has also been prepared indirectly by Piutti (*Ber.*, 1896, 29, 85) from *p*-ethoxyphenylsuccinimide (pyrantin) and caustic potash. The substance he obtained in this manner could hardly have been pure, as the melting point was stated to be 160—161°. Piutti's acid also differed from ours in its behaviour towards chlorine water, for although we were unable to obtain any coloration whatever, Piutti states that his acid gave a violet coloration with this reagent. We therefore conclude that, by the action of caustic potash on pyrantin, Piutti produced some impurity which he failed to remove entirely.

The acid is soluble in alcohol or acetic acid, but only sparingly so in dry ether. It can be precipitated by the addition of phenylhydrazine to its solution in dilute acetic acid and heating for a short time.

The sodium salt (soluble pyrantin) was also prepared, and Piutti's previous statement that it is remarkably soluble in water confirmed. Pearly leaflets separate from its aqueous solution on the addition of ammonium sulphate. Its aqueous solution immediately gives a white, curdy precipitate on the addition of silver nitrate and lead acetate, and a green, amorphous precipitate with copper sulphate. If barium nitrate be added, crystals slowly separate, and a precipitate also gradually comes down after the addition of calcium chloride.



*Methyl-p-ethoxyphenylsuccinamic Acid (Methyl-p-ethoxysuccinamic Acid),*  
 $\text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_5.$

This acid, together with the higher homologues described in this communication, were prepared in a similar manner to *p*-ethoxyphenylsuccinamic acid with the exception that benzene was used as the solvent instead of toluene. As methylsuccinic anhydride is liquid at the ordinary temperature, much less solvent was required than in the former case.

The acid separated from a 50 per cent. alcoholic solution in groups of microscopic, colourless needles melting at 149—150°. On analysis:

0.1906 gave 0.4340  $\text{CO}_2$  and 0.1156  $\text{H}_2\text{O}$ . C = 62.10; H = 6.74.

0.3028 „ 13.5 c.c. moist nitrogen at 20° and 763 mm. N = 5.57.

$\text{C}_{18}\text{H}_{17}\text{O}_4\text{N}$  requires C = 62.15; H = 6.77; N = 5.57 per cent.

The *sodium* salt is readily soluble in water. It differs somewhat from the previous salt in its action towards reagents. Amorphous precipitates were obtained with silver nitrate and copper sulphate. Lead acetate gave a copious precipitate, which dissolved in large excess, but came down again on long standing. No precipitate was obtained with barium nitrate or calcium chloride.

*as-Dimethyl-p-ethoxyphenylsuccinamic Acid (as-Dimethyl-p-ethoxysuccinamic acid),*  $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_5.$

This acid was obtained from freshly-prepared liquid *as*-dimethylsuccinic anhydride. It crystallised readily from alcohol in beautiful, small, colourless prisms melting at 160—161°, with a very slight evolution of gas. On analysis:

0.1799 gave 0.4170  $\text{CO}_2$  and 0.1184  $\text{H}_2\text{O}$ . C = 63.21. H = 7.31.

0.4120 „ 19.9 c.c. moist nitrogen at 16° and 74 mm. N = 5.36.

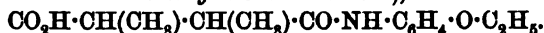
$\text{C}_{14}\text{H}_{19}\text{O}_4\text{N}$  requires C = 63.39; H = 7.17; N = 5.28 per cent.

The acid, which is only sparingly soluble in hot water, separated on cooling in thick, stumpy prisms.

The *sodium* salt was prepared in the same manner as the salts of the other acids by neutralising on the water-bath as nearly as possible with a pure normal caustic soda solution. It remained as a thick, transparent gum on heating for about 3 hours in the air oven at 140—160°. On cooling in a desiccator, it formed a transparent, brittle, hygroscopic, resinous mass. It was powdered while hot, transferred to a glass-stoppered vessel as rapidly as possible, and obtained as a white powder which became quite sticky when left for a few minutes in the open air.

Its aqueous solution gave copious precipitates with silver nitrate and copper sulphate, and more slowly with calcium chloride. Lead acetate gave a precipitate which dissolved in a large excess of the reagent. Barium nitrate only produced a slight turbidity.

*trans-s-Dimethyl-p-ethoxyphenylsuccinamic Acid (trans-s-Dimethyl-p-ethoxysuccinamic Acid),*



This acid was prepared from *trans-s*-dimethylsuccinic anhydride and *p*-phenetidine. It crystallises from alcohol in needles melting at 184—185° with slow decomposition, and is sparingly soluble in hot water, separating from the solution on cooling in prisms. On analysis:

0.2100 gave 0.4873  $\text{CO}_2$  and 0.1376  $\text{H}_2\text{O}$ .  $\text{C}=63.28$ ;  $\text{H}=7.28$ .

0.3206 „ 16 c.c. moist nitrogen at 17° and 760 mm.  $\text{N}=5.81$ .

$\text{C}_{14}\text{H}_{19}\text{O}_4\text{N}$  requires  $\text{C}=63.39$ ;  $\text{H}=7.17$ ;  $\text{N}=5.28$  per cent.

The *sodium* salt gave colloidal precipitates with silver nitrate and copper sulphate. The precipitate given by lead acetate dissolved in a large excess of the reagent, but separated out again on standing. No precipitate was obtained with barium nitrate or calcium chloride.

*cis-Dimethyl-p-ethoxyphenylsuccinamic Acid (cis-Dimethyl-p-ethoxysuccinamic Acid),*  $\text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_5.$

This compound crystallised from alcohol in warty groups consisting of microscopic needles which did not readily separate from the solvent on the filter pump and melted at 155—156°. On analysis:

0.1500 gave 0.3479  $\text{CO}_2$  and 0.0989  $\text{H}_2\text{O}$ .  $\text{C}=63.26$ ;  $\text{H}=7.33$ .

0.2688 „ 12.2 c.c. moist nitrogen at 11° and 758 mm.  $\text{N}=5.39$ .

$\text{C}_{14}\text{H}_{19}\text{O}_4\text{N}$  requires  $\text{C}=63.39$ ;  $\text{H}=7.17$ ;  $\text{N}=5.28$  per cent.

The pure *sodium* salt was *not* obtainable under the conditions adopted. On attempting to neutralise the hot solution of the acid and evaporating down somewhat, a small quantity of crystals separated. After filtration, the aqueous solution had a slightly alkaline reaction and no further attempt to isolate this salt was undertaken.

The crystals which separated were collected, washed, and dried on a porous plate. They then melted at 112—113°. On cooling the hot aqueous solution, they separated in crystalline groups of sandy appearance, which under the microscope were seen to consist of ball-shaped groups of needles.

As *cis*-dimethylpyrantin melts at 114—115° and crystallises similarly, there can be no doubt that under these conditions a portion of the salt condenses to the ring compound in preference to remaining as the sodium salt of the open-chain acid.

So far as the observations went, this salt differs from the *trans*-sodium salt, as with the latter no crystals of a ring compound separated on evaporation of the aqueous solution of the salt.

*Trimethyl-p-ethoxyphenylsuccinamic Acid (Trimethyl-p-ethoxysuccinanic Acid)*,  $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_5$ .

This acid crystallised from alcohol in warty groups of colourless plates or prisms melting at 128—129°, which were sparingly soluble in water. On analysis:

0.1462 gave 0.3448  $\text{CO}_2$  and 0.1012  $\text{H}_2\text{O}$ . C = 64.31; H = 7.69.

0.3921 „ 17.95 c.c. moist nitrogen at 18° and 753 mm. N = 5.21.

$\text{C}_{15}\text{H}_{21}\text{O}_4\text{N}$  requires C = 64.51; H = 7.52; N = 5.02 per cent.

On allowing the mother liquors from the above recrystallisations to evaporate spontaneously, a further considerable quantity of the crystalline substance separated. This differed from the compound which had already separated in that it melted at 86—88°, and was obtained in the form of needles. After recrystallisation from acetic acid, it again melted at 87—88°, and was found to be *trimethylpyrantin*.

As in the case of the *cis*-dimethyl-p-ethoxyphenylsuccinamic acid, a pure sodium salt could not be obtained under the conditions employed. When the acid was neutralised and the solution evaporated, crystals of trimethylpyrantin melting at 87—88° were obtained, and the solution became alkaline. When the solution was evaporated down, and the residue dried at 140—150° and digested with water, a crystalline mass remained behind, and the solution was found to be strongly alkaline to litmus. On recrystallising this insoluble portion from dilute acetic acid, it separated in needles melting at 86—88°, and was therefore nothing more or less than *trimethylpyrantin*. Under these circumstances, no further attempts were made to prepare the sodium salt.

*isoPropyl-p-ethoxyphenylsuccinamic Acid (isoPropyl-p-ethoxysuccinanic Acid)*,  $\text{CO}_2\text{H}\cdot\text{CH}[\text{CH}(\text{CH}_3)_2]\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_5$ .

This acid crystallised from alcohol in beautiful, transparent leaflets, which had a pearly lustre when dry and melted at 151—152°. It gave a faintly acid aqueous solution. On analysis:

0.1901 gave 0.4478 CO<sub>2</sub> and 0.1306 H<sub>2</sub>O. C=64.26; H=7.63.

0.2819 „ 12.5 c.c. moist nitrogen at 17° and 763 mm. N=5.16.

C<sub>15</sub>H<sub>21</sub>O<sub>4</sub>N requires C=64.51; H=7.52; N=5.02 per cent.

The pure sodium salt was not prepared, as on attempting to neutralise the acid on a water-bath and to crystallise the product a large amount of *isopropylpyrantin* was obtained.

## II. The Pyrantins.



When heated above its melting point, *p*-ethoxyphenylsuccinamic acid readily parts with 1 mol. of water, the general method of preparation of pyrantin and its homologues being to warm the corresponding acid at about 180° in a sulphuric acid bath for about 40 minutes or until the evolution of aqueous vapour ceased. The product, which in most cases had darkened slightly in colour, was poured into a dilute solution of sodium carbonate to dissolve out any unattacked acid, and the resulting nearly colourless and brittle product filtered off, washed with water, and recrystallised from a little glacial acetic acid to remove small traces of colouring matter, and then from alcohol, from which it separated readily in colourless needles melting at 155°.

This substance has been previously prepared by Piutti (*loc. cit.*) by the direct condensation of *p*-aminophenetole hydrochloride or phenacetin with succinic acid, and its melting point given as about 155°.

We also prepared this substance and its homologues by the direct interaction of succinic or an alkyl-succinic acid and *p*-phenetidine at temperatures of about 160—180°. In all cases, the reaction was very vigorous, and the product readily solidified on cooling. To purify it, the substance was dissolved in the least possible quantity of glacial acetic acid, the solution cooled, and the crystalline mass spread on a porous plate. The coloured matter was thus absorbed and a second treatment, if necessary, followed by a recrystallisation, always yielded a colourless product.

As obtained in this way, pyrantin melted at 155°. Its solubility was determined in a 0.75 per cent. solution of sodium chloride at 30° as best representing conditions in the human system to which the drug would have to be subjected if employed internally. It was found that only 0.0701 gram dissolved in 50 c.c. of the solution, which gives the ratio 1:713.

The colourless crystals (m. p. 155°), after being carefully dried for about 20 minutes at 97°, were analysed, with the following results:

0.1996 gave 0.4771 CO<sub>2</sub> and 0.1050 H<sub>2</sub>O. C=65.20; H=5.90.

0.2922 „ 16.6 c.c. moist nitrogen at 21° and 765 mm. N=6.52.

C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>N requires C=65.75; H=5.93; N=6.39 per cent.

The measurement of the stability of the succinimide ring was carried out by a slightly modified form of the method employed by Hantzsch

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{x}{A - x}$	<i>Ac.</i>
(1.) <i>A</i> = 10.20.				
12	5.61	4.59	1.2222	0.1018
15	5.67	4.63	1.2030	0.0802
18	6.66	3.64	1.8022	0.1001
21	6.31	3.89	1.6221	0.0772
24	7.86	2.84	2.6916	0.1079
27	7.55	2.65	2.8492	0.1055
				Mean 0.0984
(2.) <i>A</i> = 10.20.				
6	4.20	6.00	0.7000	0.1166
9	4.97	5.23	0.9503	0.1056
12	5.83	4.87	1.0945	0.0912
15	6.13	4.07	1.5061	0.1004
18	6.24	3.96	1.5757	0.0875
21	6.73	3.47	1.9395	0.0923
24	7.00	3.20	2.1875	0.0911
27	7.44	2.76	2.6956	0.0998
				Mean 0.0981
(3.) <i>A</i> = 9.40.				
12	4.90	4.5	1.0888	0.0907
14	4.90	4.5	1.0888	0.0777
16	5.30	4.1	1.2927	0.0808
18	6.10	3.3	1.8484	0.1027
20	6.20	3.2	1.9375	0.0969
21½	6.40	3.0	2.1333	0.0992
				Mean 0.0913

The mean of the three series of determinations is *Ac* = 0.0949.

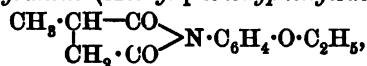
and Miolati (*loc. cit.*). Alcohol had to be used as the solvent on account of the sparing solubility of the homologues of pyrantin in water.

0.2190 gram of pyrantin was dissolved in 190 c.c. of alcohol; the

solution was allowed to stand in the thermostat for about a quarter of an hour at 25°, and then 10 c.c. of a *N*/10 caustic soda solution were added. Twenty c.c. were then withdrawn at regular known intervals and titrated with *N*/100 hydrochloric acid, using phenolphthalein as indicator. Under these conditions, 10 c.c. of *N*/100 standard acid solution should correspond exactly to the amount of caustic soda which would be present in the 20 c.c. withdrawn for titration if no opening of the ring had taken place.

The results (p. 794) were calculated from the formula  $Ac = \frac{1}{t} \cdot \frac{x}{A-x}$  already used for phenyl-, tolyl-, and xylyl-succinimides by Miolati and Longo (*loc. cit.*), where *A* represents the amount of substance present at the commencement of the reaction, *x* is the amount of the changed substance present after time *t* (in minutes), and *c* is a constant. In this and the estimations which follow *A* = 10 nearly.

*Methylpyrantin* (*Methyl-p-ethoxyphenylsuccinimide*),



was crystallised first from glacial acetic acid and then from alcohol. It separated from the latter solvent in small clusters of flat prisms melting at 105—106°. Crystals having the same melting point were also obtained by melting the crude substance in alcohol, adding hot water to the warm solution until it became slightly turbid, and then allowing it to cool, but the methylpyrantin obtained in this manner had a slight greyish tinge. On analysis:

0.2109 gave 0.5176 CO<sub>2</sub> and 0.1270 H<sub>2</sub>O. C = 67.0; H = 6.7.

0.4106 „ 21.9 c.c. moist nitrogen at 18° and 754 mm. N = 6.09.

C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>N requires C = 66.96; H = 6.43; N = 6.00 per cent.

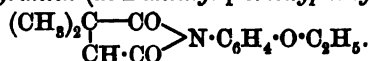
It is only moderately soluble in hot water and separates in needles on cooling; 0.0694 gram dissolved in 50 c.c. of 0.75 per cent. sodium chloride solution under the conditions given above for pyrantin gave the ratio 1 : 720.

For the determination of the stability constant, as described above, 0.2330 gram was required to make *A* = 10.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{x}{A - x}$	<i>Ac.</i>
(1.) <i>A</i> = 10·20.				
8	4·32	5·88	0·7347	0·2549
6	5·79	4·41	1·3129	0·2188
9	6·20	4·00	1·5500	0·1722
12	6·80	3·40	2·0000	0·1666
15	7·24	2·96	2·4459	0·1631
18	7·78	2·44	3·1803	0·1767
21	7·78	2·42	3·2149	0·1531
24	8·05	2·15	3·7542	0·1560
27	8·42	1·78	4·7303	0·1752
				Mean 0·1807
(2.) <i>A</i> = 10·20.				
4	4·94	5·26	0·9391	0·2348
7·5	5·79	4·41	1·3129	0·1750
10	6·09	4·11	1·4817	0·1482
12·5	7·30	2·90	2·5172	0·2013
15·5	7·36	2·84	2·5915	0·1672
18	7·60	2·60	2·9231	0·1624
21	8·14	2·06	3·9514	0·1881
23·5	8·27	1·93	4·2850	0·1823
26·5	8·65	1·55	5·5806	0·2106
				Mean 0·1855

The mean of the two series of experiments is *Ac* = 0·1831.

*as*-Dimethylpyrantin (*as*-Dimethyl-*p* ethoxyphenylsuccinimide),



The *as*-dimethyl-*p*-ethoxyphenylsuccinamic acid used in the preparation of *as*-dimethylpyrantin effervesced very strongly as it melted, and as the product seemed to darken rather rapidly and the reaction appeared to be complete after about 20 minutes' heating at 180°, the viscid liquid was at once slowly poured into a dilute sodium carbonate solution. It did not crystallise out at all readily from alcohol until a crystal of the substance had been added; colourless needles were then obtained melting at 73°. This pyrantin was also prepared by the direct method of heating together the equivalent amounts of *as*-dimethylsuccinic acid and *p*-phenetidine. The specimen obtained melted at 70—72°. On analysis :

0.1470 gave 0.3658 CO<sub>2</sub> and 0.0926 H<sub>2</sub>O. C = 67.88; H = 7.00.

0.4002 „ 20.5 c.c. moist nitrogen at 19° and 750 mm. N = 5.80.

C<sub>14</sub>H<sub>17</sub>O<sub>3</sub>N requires C = 68.03; H = 6.88; N = 5.67 per cent.

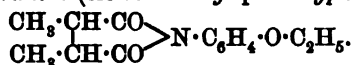
0.0502 gram of the compound dissolved in 50 c.c. of 0.75 per cent. sodium chloride solution giving the ratio 1 : 996. It is only very moderately soluble in hot water, from which it separated in needles.

For the determination of the stability constant, 0.2470 gram was required to make A = 10.

<i>t</i> .	<i>z</i> .	<i>A - z</i> .	$\frac{z}{A - z}$	<i>Ac</i> .
(1.) <i>A</i> = 10.20.				
6	4.31	5.89	0.7817	0.1219
9	4.68	5.52	0.8478	0.0942
12	5.16	5.04	1.0238	0.0853
15	5.44	4.76	1.1428	0.0762
18	6.08	4.12	1.4514	0.0806
21	6.29	3.91	1.6087	0.0766
24	6.61	3.59	1.8412	0.0767
27	7.00	3.20	2.1875	0.0810
				Mean 0.0866
(2.) <i>A</i> = 10.20.				
9	4.85	5.35	0.9065	0.1007
12	5.60	4.60	1.2174	0.1014
15	5.75	4.45	1.2919	0.0861
18	6.02	4.18	1.4402	0.0800
21	6.24	3.96	1.5757	0.0750
24	6.81	3.39	2.0088	0.0837
				Mean 0.0878

The mean of the two series is *Ac* = 0.0872.

*cis-s*-Dimethylpyrantin (*cis-s*-Dimethyl-*p*-ethoxyphenylsuccinimide),



After having been crystallised from acetic acid, *cis-s*-dimethylpyrantin separated from alcohol as a mass of small needles, which had a silky appearance when dry and melted at 114—115°. It was also obtained in small quantity during the attempts to prepare the sodium salt of *cis-s*-dimethyl-*p*-ethoxyphenylsuccinamic acid (p. 791). On analysis :



0.1841 gave 0.4953  $\text{CO}_2$  and 0.1130  $\text{H}_2\text{O}$ . C = 68.42; H = 68.3.

0.2806 „ 14.35 c.c. moist nitrogen at  $11^\circ$  and 762 mm. N = 5.81.

$\text{C}_{14}\text{H}_{17}\text{O}_5\text{N}$  requires C = 68.03; H = 6.88; N = 5.67 per cent.

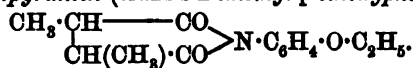
0.0543 gram of the substance dissolved in 50 c.c. of 0.75 per cent. sodium chloride solution, giving a solubility ratio of 1:920. It is only moderately soluble in hot water, separating out in needles on cooling.

For the determination of the stability constant 0.2470 gram was required to make  $A = 10$ .

$t$ .	$x$ .	$A - x$ .	$\frac{x}{A - x}$ .	$Ac$ .
(1.) $A = 10.20$ .				
6	5.09	5.11	0.9961	0.1660
9	5.77	4.43	1.3025	0.1447
12	6.40	3.80	1.6843	0.1404
15	6.76	3.44	1.9651	0.1310
18	7.15	3.08	2.3443	0.1302
21	7.41	2.79	2.6558	0.1265
24	7.79	2.41	3.2323	0.1347
27	8.03	2.17	3.7005	0.1371
30	8.19	2.01	4.0746	0.1358
				Mean 0.1385
(2.) $A = 10.20$ .				
6	5.11	5.09	1.0039	0.1673
9	5.59	4.61	1.2126	0.1336
12	6.49	3.71	1.7499	0.1458
15	6.81	3.39	2.0088	0.1339
18	7.21	2.99	2.4113	0.1339
21	7.51	2.69	2.7913	0.1328
24	7.69	2.51	3.0637	0.1276
				Mean 0.1393

The mean of the two series is  $Ac = 0.1389$ .

*trans-s-Dimethylpyrantin* (*trans-s-Dimethyl-p-ethoxyphenylsuccinimide*),

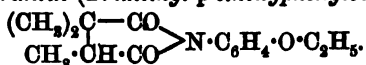


As *trans-s*-dimethyl-*p*-ethoxyphenylsuccinamic acid melts at  $184-185^\circ$ , a temperature of  $190-195^\circ$  was employed in the condensation, and maintained until the evolution of aqueous vapour had ceased. After the

usual treatment with acetic acid and alcohol, colourless needles melting at 104—105° were obtained, a temperature which is 10° lower than that at which the *cis*-compound melts. A couple of recrystallisations did not alter the melting point.

*trans-s*-Dimethylsuccinic acid is easily converted into the *cis*-modification by simple heating; it might therefore be expected that in an analogous manner a *cis*-pyrantin derivative, or at least a mixture of the *cis*- and *trans*-compounds, would be obtained, and the low melting point also lends colour to this possibility. As, however, a determination of the stability constant gave figures which are completely different from those of the *cis-s*-dimethylpyrantin, the results are published here, and the definite solution of the problem as to whether the substance was pure *trans-s*-dimethylpyrantin or a mixture of the two modifications must be postponed to a future occasion. The stability constant obtained with the material we had at our disposal gave a mean for one series of experiments of 0.1839.

*Trimethylpyrantin (Trimethyl-p-ethoxyphenylsuccinimide),*



Trimethylpyrantin has been isolated in several ways, as the ring compound is formed with remarkable readiness. Thus it is obtained (1) by heating trimethyl-*p*-ethoxyphenylsuccinamic acid to 180°; (2) in large quantity in the alcoholic mother liquors from the recrystallisation of the acid, especially on standing; (3) from the alkaline solution produced on attempting to prepare sodium trimethyl-*p*-ethoxyphenylsuccinamate; (4) on dissolving trimethyl-*p*-ethoxyphenylsuccinamic acid in dilute caustic soda and allowing the solution to stand, when beautiful leaflets gradually separate out, and (5) by heating together equivalent quantities of *p*-phenetidine and trimethylsuccinic acid. After recrystallisation from acetic acid followed by alcohol, it separates in colourless needles melting at 87—88°. On analysis:

0.1802 gave 0.4562 CO<sub>2</sub> and 0.1218 H<sub>2</sub>O. C = 69.06; H = 7.51.

0.1992 „ 9.4 c.c. moist nitrogen at 22° and 746 mm. N = 5.50.

C<sub>15</sub>H<sub>19</sub>O<sub>5</sub>N requires C = 68.96; H = 7.28; N = 5.36 per cent.

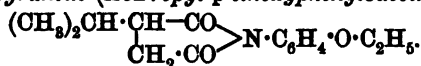
It is only very sparingly soluble in 0.75 per cent. sodium chloride solution, 0.0394 gram dissolving in 50 c.c., which gives the ratio 1:1272. In boiling water, it is almost insoluble, and the little that dissolves crystallises out again on cooling in hair-like needles.

For the determination of the stability constant, 0.2610 gram was required to make  $A = 10$ ,

$t$	$x$	$A - x$	$\frac{x}{A - x}$	$\Delta c$
(1.) $A = 10.20$ .				
9	3.35	6.85	0.4890	0.0548
13	3.65	6.55	0.5573	0.0429
17	4.08	6.12	0.6666	0.0392
21	4.90	5.30	0.9245	0.0440
25	5.00	5.20	0.9615	0.0385
29	5.04	5.16	0.9767	0.0337
33	5.38	4.82	1.1162	3.0338
37	6.22	3.98	1.5628	0.0422
41	6.36	3.84	1.6562	0.0404
				Mean 0.0410
(2.) $A = 10.20$ .				
10	3.60	6.60	0.5454	0.0545
20	4.60	5.60	0.8214	0.0411
30	5.20	5.00	1.0400	0.0347
40	5.85	4.35	1.3448	0.0386
55	7.30	2.90	2.5172	0.0458
				Mean 0.0419
(3.) $A = 10.20$ .				
11	3.80	6.40	0.5937	0.0540
15	4.25	5.95	0.7143	0.0476
19	4.62	5.58	0.8280	0.0436
23	5.39	4.81	1.1206	0.0487
27	5.32	4.88	1.0901	0.0404
31	6.54	3.66	1.7870	0.0576
35	6.51	3.69	1.7642	0.0504
				Mean 0.0489
(4.) $A = 10.20$ .				
9	3.37	6.83	0.4934	0.0548
12	3.70	6.50	0.5602	0.0474
15	4.22	5.98	0.7056	0.0470
18	4.53	5.67	0.7989	0.0444
21	4.92	5.28	0.9318	0.0473
24	5.28	4.92	1.0731	0.0447
27	5.39	4.81	1.1205	0.0415
				Mean 0.0467

The mean of the four series is  $\Delta c = 0.0446$ .

*isoPropylpyrantin (isoPropyl-p-ethoxyphenylsuccinimide),*



This compound crystallised from alcohol in colourless, glistening needles melting at 98—99°. In addition to the ordinary mode of preparation, it was obtained in large quantity during the attempts to prepare a pure sodium salt from the *isopropyl-p-ethoxyphenylsuccinamic acid* (p. 793); it then melted at 97°. On analysis:

0.1980 gave 0.4988 CO<sub>2</sub> and 0.1338 H<sub>2</sub>O. C = 68.70; H = 7.51.

0.4208 „ 20.4 c.c. moist nitrogen at 20° and 763 mm. N = 5.56.

C<sub>18</sub>H<sub>19</sub>O<sub>3</sub>N requires C = 68.96; H = 7.28; N = 5.36 per cent.

It is very sparingly soluble in the 0.75 per cent. salt solution, 0.0451 gram dissolving in 50 c.c., thus giving the ratio of 1 : 1110. It is only moderately soluble in boiling water and separates out in long needles on cooling.

For the determination of the stability constant, 0.2610 gram was required to make A = 10.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{x}{A - x}$	<i>Ac.</i>
(1.) <i>A</i> = 10.20.				
8	5.42	4.78	1.1389	0.1417
11	5.90	4.30	1.3721	0.1247
14	6.90	3.30	2.0909	0.1493
17	7.28	2.92	2.4981	0.1466
20	7.44	2.76	2.6956	0.1348
23	7.81	2.39	3.2678	0.1421
26	8.27	1.93	4.2850	0.1646
				Mean 0.1434
(2.) <i>A</i> = 10.20.				
6	5.17	5.08	1.0278	0.1718
9	5.78	4.43	1.3077	0.1453
12	6.12	4.08	1.5000	0.1250
15	6.94	3.26	2.1288	0.1419
18	7.23	2.97	2.4343	0.1352
21	7.54	2.66	2.8346	0.1350
24	7.92	2.28	3.4737	0.1447
27	8.17	2.03	4.0246	0.1491
				Mean 0.1434

The mean of the two series is *Ac* = 0.1434.



This compound was prepared in the usual manner, and its stability constant was determined in both alcoholic and aqueous solution.

Three series of experiments were carried out in alcoholic solution with the following results :

$t.$	$x.$	$A - x.$	$\frac{x}{A - x}$	$\Delta c.$
(1.) $A = 9.56.$				
7	3.34	6.22	0.5370	0.0767
9	3.68	5.88	0.6259	0.0695
12	4.46	5.10	0.8745	0.0729
16	4.86	5.20	0.8387	0.0524
18.5	4.72	4.84	0.9752	0.0527
21	4.54	5.02	0.9044	0.0431
24.5	4.83	4.73	1.0212	0.0417
28	4.95	4.61	1.0738	0.0383
32	5.86	3.70	1.5840	0.0495
				Mean 0.0552
(2.) $A = 10.20.$				
9	3.66	6.54	0.5596	0.0622
12	4.20	6.00	0.7000	0.0583
15	4.55	5.65	0.8053	0.0537
18	5.14	5.06	1.0158	0.0564
21	5.23	4.97	1.0523	0.0501
24	5.54	4.66	1.1888	0.0497
27	6.31	3.89	1.6195	0.0599
				Mean 0.0557
(3.) $A = 9.56.$				
5.75	2.86	6.70	0.4269	0.0742
10	3.60	5.96	0.6040	0.0604
12.75	3.91	5.65	0.6920	0.0543
15.25	4.22	5.34	0.7903	0.0518
19	4.76	4.80	0.9917	0.0522
21.75	5.11	4.45	1.1483	0.0528
25.25	5.21	4.35	1.1977	0.0474
29.5	6.00	3.56	1.6854	0.0571
				Mean 0.0563

The mean of the three series is  $\Delta c = 0.0557.$

To obtain a means of comparing the results obtained above for the methylpyrantins with the tolyl- and xylyl-succinimides, it was necessary to know the stability constant of phenylsuccinimide in aqueous solution. This determination has already been made by Miolati and Longo (*Atti R. Accad. Lincei*, 1894, [v], 3, 601), but unfortunately there is an error in the calculations. These authors give the mean of three series of experiments as 2.27, but if the mistake in the first series be rectified, the mean works out to be 2.18.

Two series of experiments were also carried out with phenylsuccinimide in aqueous solution, with the following results:

$t$	$x$	$A - x$	$\frac{x}{A - x}$	$\Delta c$
(1.) $A = 9.56$ .				
3.3	8.09	1.47	5.485	1.5848
4.4	8.76	0.8	10.950	2.4886
5.5	8.96	0.6	14.933	2.7140
6.6	8.91	0.65	13.708	2.0770
9.9	9.16	0.4	22.900	2.8131
				Mean 2.2551
(2.) $A = 9.56$ .				
3.0	8.26	1.3	6.354	2.1180
4.25	8.76	0.8	10.950	2.5765
5.25	8.81	0.75	11.747	2.2375
6.25	8.91	0.65	13.708	2.1933
7.25	9.06	0.50	18.120	2.4965
9	9.14	0.42	21.762	2.4180
11	9.20	0.36	25.555	2.3232
				Mean 2.3375

The mean of the two series is  $\Delta c = 2.29$ .

If the mean of Miolati and Longo's and of the authors' experiments be taken as probably the most correct figure, namely  $\Delta c = 2.23$ , the values for the substituted pyrantins in alcoholic solution can be first converted into the corresponding values for the respective substituted phenylsuccinimides in the same solvent, and then the value of the latter compounds converted from the stability constant,  $\Delta c$ , in alcoholic to that in aqueous solution.

The experimental data necessary to accomplish this have been determined above with pyrantin in alcoholic solution and with phenylsuccinimide in both alcoholic and aqueous solution.

The pyrantin was found to have a stability constant,  $A_c = 0.0949$ , and phenylsuccinimide one of  $A_c = 0.0557$ , so although the ethoxyl group is so far away as the para-position to the nitrogen in the succinimide ring, it has a very great effect in decreasing the stability of the fatty nucleus.

The two measurements give a factor  $\frac{0.0557}{0.0949}$  (or divide by 1.704) for the conversion of the values of the substituted pyrantins into those of the corresponding phenylsuccinimides.

*In Alcoholic Solution.*

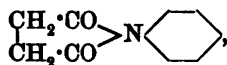
	$A_c$ found.		$A_c$ calc.
Pyrantin .....	0.0949	Phenylsuccinimide .....	0.0557
Methylpyrantin .....	0.1831	Methylphenylsuccinimide	0.1075
<i>as</i> -Dimethylpyrantin ...	0.0872	<i>as</i> -Dimethylphenylsuccinimide .....	0.0512
<i>cis-s</i> -Dimethylpyrantin...	0.1389	<i>cis-s</i> -Dimethylphenylsuccinimide.....	0.0815
<i>trans-s</i> -Dimethylpyrantin (0.1839 †)		<i>trans-s</i> -Dimethylphenylsuccinimide .....	(0.1079 †)
Trimethylpyrantin .....	0.0446	Trimethylphenylsuccinimide .....	0.0262
<i>iso</i> Propylpyrantin .....	0.1432	<i>iso</i> Propylphenylsuccinimide .....	0.0840

The stability constant,  $A_c$ , for phenylsuccinimide in alcoholic solution being 0.0557, and in aqueous solution 2.23, we get the second factor for the conversion of the value in alcoholic to that in aqueous solution, namely, 40.03, since  $0.0557 \times 40.03 = 2.23$ , giving the following results :

	Constant calculated	
	for alcoholic solution.	for aqueous solution.
Phenylsuccinimide .....	0.0557 (found)	2.23 (found)
Methylphenylsuccinimide.....	0.1075	4.30
<i>as</i> -Dimethylphenylsuccinimide .....	0.0512	2.05
<i>cis-s</i> -Dimethylphenylsuccinimide .....	0.0815	3.26
<i>trans-s</i> -Dimethylphenylsuccinimide...	(0.1079 †)	(4.32 †)
Trimethylphenylsuccinimide .....	0.0262	1.05
<i>iso</i> Propylphenylsuccinimide .....	0.0840	3.36

The values so obtained, in conjunction with the experimental data of Miolati and his colleagues, enable a comparison to be made of the

result of an introduction of the methyl group into almost any position in the phenylsuccinimide ring,



and such comparison is afforded in the following list :

	<i>Ac.</i>		<i>Ac.</i>
<i>trans-s</i> -Dimethylphenyl-			
succinimide .....	(4.32 †)	Xylylsuccinimide .....	1.145
Methylphenylsuccinimide .....	4.30	<i>p</i> -Tolylsuccinimide .....	1.12
<i>iso</i> Propylphenylsuccin-			
imide .....	3.36	<i>m</i> -Tolylsuccinimide .....	1.10
<i>cis-s</i> -Dimethylphenylsuc-			
cinimide .....	3.27	Trimethylphenylsuccinimide .....	1.05
Phenylsuccinimide .....	2.23	2:5-Xylylsuccinimide .....	0.88
<i>as</i> -Dimethylphenylsuccin-			
imide .....	2.05	<i>o</i> -Tolylphenylsuccinimide...	0.856
3:4-Xylylsuccinimide.....	1.27	2:3-Xylylsuccinimide .....	0.815
		2:6-Xylylsuccinimide, 0.16.	

### III. Conclusions.

The general conclusions to be drawn from the data obtained in this research would seem to be as follows for phenylsuccinimide and similarly constituted substances.

(1) Methyl groups introduced into an aromatic ring which is linked to an imide ring by means of the nitrogen atom cause the latter to become more stable ; also the nearer the methyl group is to the nitrogen atom the more stable is the ring (compare work of Miolati and his colleagues).

(2) A methyl group introduced into the imide ring renders that ring less stable, but on the introduction of more methyl groups the stability increases, and after a certain number have been introduced, the stability becomes greater than in the case of the ring which does not contain the methyl group.

(3) For a corresponding number of methyl groups, a substance containing constituents in the aromatic ring is much more stable than one with substituents in the imide ring.

(4) The introduction of an ethoxyl group into the para-position in the aromatic ring causes a great decrease in the stability of the imide ring.

The deductions could not be carried further without completing the experimental study of the effect of introducing methyl groups in both the aromatic and imide rings at the same time. One or two other interest-



ing points had also to be left in an incomplete state owing to the authors leaving Owens College, where the practical part of the work was carried out; it was therefore decided to publish the results obtained.

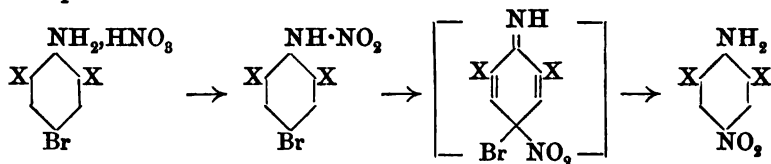
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### LXXXI.—*The Preparation of Highly Substituted Nitroaminobenzenes.*

By K. J. P. ORTON.

In the action of nitric acid on *s*-trihalogen anilines (this vol., p. 490), the nitroamino-*s*-trihalogen benzenes are always formed in small amount. These nitroamines, under appropriate conditions, yield products identical with those obtained by the direct action of nitric acid on the anilines. It was suggested (*loc. cit.*) that possibly the following series of changes took place:



The final transformation only occurs when a bromine atom is in the para-position relatively to the amino-group. When a chlorine atom is in the para-position, the iminoquinone, if formed, undergoes change in some other manner.\*

In order to study more minutely the transformations of these nitroamino-*s*-trihalogen benzenes, it was necessary to devise means of readily preparing them in quantity. The methods at present known (Bamberger, *Ber.*, 1893, 26, 471, 485; 1894, 27, 584; 1895, 28, 401) of preparing nitroaminobenzenes are (1) oxidation of alkaline solutions of diazotates by potassium ferricyanide or permanganate; (2) addition of dry aniline nitrate to acetic anhydride; (3) treatment of the aniline in solution in ether or chloroform with nitrogen pentoxide. Owing

\* It is doubtful if in the nitration of anilines and anilides it is justifiable to assume that the nitroamino-derivatives necessarily occur as an intermediate stage. The course followed by the reaction must depend on whether, under the given conditions, the velocity of the formation of the nitroamino-derivative exceeds that of the direct action of the nitric acid with the aniline (or anilide) or with its tautomeric (iminoquinone) form. The same considerations apply to the chlorination and bromination of anilines and anilides.

to the feeble basic characters of the *s*-trihalogen anilines, the first two methods could only be applied with difficulty, and the use of nitrogen pentoxide is attended by many obvious disadvantages.

I have found that the *s*-trisubstituted anilines (*s*-tribromoaniline, 3:5-dibromotoluidines, &c.) can be converted with ease and practically quantitatively into nitroamino-derivatives when a solution (or suspension) of the aniline in glacial acetic acid is treated successively with some excess of nitric acid (free from nitrous acid) and acetic anhydride. The nitrate of the aniline, first formed, rapidly goes into solution, being converted nearly completely into the nitroamine. There is some development of heat in the reaction. The method is also applicable to anilines in which one ortho-position is occupied by hydrogen (for example, 2:4-dichloroaniline); in this case, the conversion of nitrate into nitroamine does not take place so easily, and some nitration of the aniline in the ortho-position also occurs. With *p*-halogen anilines, the formation of the nitroamine from the nitrate is still more difficult, and is accompanied by more nitration.

The nitroamino-*s*-trihalogen benzenes, which have a bromine atom in the para-position relatively to the imino-group, are largely converted into dihalogen-*p*-nitroanilines (compare this vol., p. 491), when their solutions in acetic acid, to which a drop of sulphuric acid has been added, are allowed to stand for several hours. With 2-nitroamino-3:5-dibromotoluene and 1-nitroamino-2:4:6-tribromo-3-nitrobenzene, the replacement of the *p*-bromine atom by the nitro-group scarcely appears to take place under these conditions.

When added to concentrated sulphuric acid, the majority of the nitroaminobenzenes here described give a deep purple or violet solution, with development of heat; if the sulphuric acid contains a little water, the solution is much paler and magenta-coloured. So long as a rise of temperature is avoided, only a small quantity of the oxides of nitrogen is evolved. Bromine is given off if a *p*-bromine atom is present. When a nitroamine containing an *o*-hydrogen atom is dissolved in sulphuric acid and the purple solution poured on to ice, the colour changes sharply to yellow, and a yellow precipitate of the isomeric nitrated aniline is thrown down; thus nitroamino-2:4-dichlorobenzene is nearly entirely converted into 2:4-dichloro-6-nitroaniline in this way. When the purple solution of a nitroamino-*s*-trihalogen benzene containing a *p*-bromine atom (*s*-tribromoaniline, &c.) is poured on to ice, the colour changes to red and a red precipitate is thrown down; this precipitate contains a small amount of the dihalogen-*p*-nitroaniline and a well crystallised, red substance, probably nearly related to the substances obtained by the action of nitric acid on *s*-dihalogen-*p*-chloroanilines (*loc. cit.*). If the nitroamino-*s*-trihalogen benzene contains a *p*-chlorine atom, its behaviour resembles that of the last case, except that no

chlorine or bromine is evolved and no *p*-nitrated aniline formed. The products, whether *s*-dihalo-nitroanilines or red substances, obtained by pouring these purple solutions on to ice, dissolve in concentrated sulphuric acid; they no longer give a deep purple coloration, but produce respectively a yellow or reddish-brown solution. Further, as above mentioned, the nitroamino-derivative of 2:4-dichloroaniline under this treatment yields 2:4-dichloro-6-nitroaniline nearly quantitatively. Hence, it seems highly probable that the purple solution corresponds to an intermediate stage between the nitroamine and the nitrated aniline.

In the ordinary nitration of anilines in the presence of a large excess of sulphuric acid (for example, in the nitration of *m*-bromoaniline, this vol., p. 499), a purple solution is formed, which changes to yellow on pouring the acid liquor on to ice.

Concentrated nitric acid (sp. gr. 1.5) readily dissolves the nitroamines, producing a solution which is more or less transiently of a purple colour; the nitroamines derived from tetra-substituted anilines (2:3:4:6-tetrabromoaniline, &c.) give only a brown solution.

#### EXPERIMENTAL.

**1-Nitroamino-2:4:6-tribromobenzene,**  $C_6H_2Br_3 \cdot NH \cdot NO_2$ .—Thirty grams of finely powdered *s*-tribromoaniline were suspended in 300 c.c. of cold glacial acetic acid\* (m. p.  $15.5^\circ$ ). Twenty-five to 30 c.c. of nitric acid (sp. gr. 1.5) free from nitrous acid were then added, and 30 c.c. of acetic anhydride slowly poured in, while the mixture was kept cold and well stirred. The solid slowly and completely dissolved, forming a solution of a pale reddish or magenta colour. The liquid was now poured on to about 600 grams of ice and water; a copious buff precipitate appeared, which was collected, washed free from acid, and then extracted with a cold solution of 10 grams of sodium carbonate in 150 c.c. of water. The solid nearly completely dissolved, leaving 2 grams of a yellow substance, consisting mainly of *s*-tribromoaniline together with a little 2:6-dibromo-4-nitroaniline. The colourless alkaline solution, after filtration, was diluted to 2 or 3 litres, warmed to about  $80^\circ$ , and then slowly acidified with a slight excess (about 100 c.c.) of 10 per cent. hydrochloric acid. The hot liquid, from which the nitroamine separated in small, slender needles, was rapidly cooled and the solid collected and dried. It weighed 31 grams.

Although the needles appear to be colourless in suspension in the mother liquor, they are found to be flesh-coloured when in mass. They can be obtained free from all colour by carefully acidifying a

\* It is inadvisable to use sufficient acetic acid to completely dissolve this sparingly soluble aniline.

dilute lukewarm solution of the barium salt. The nitroamines derived from *s*-trisubstituted anilines seem to have a greater tendency to become coloured than other nitroaminobenzenes (see nitroamino-2:4-dichlorobenzene), and their solutions in organic solvents deposit coloured crystals.

This substance, thus prepared, melted and decomposed at  $143^{\circ}$ , and was in every respect identical with the specimen previously obtained by the action of nitric acid on *s*-tribromoaniline (this vol., p. 493). It can be titrated by *N*/10 potassium hydroxide in the presence of phenolphthalein :

0.3368 neutralised 9.18 c.c. *N*/10 KOH. Equivalent = 366.8.

$C_6H_3O_2N_2Br_3$  requires equivalent = 375.

The *silver* salt is a white, insoluble powder insensitive to light.

The *barium* salt is prepared by mixing warm solutions of barium chloride and the ammonium salt, when it immediately separates in lustrous plates. On analysis of the air-dried salt :

0.9684, at  $100^{\circ}$ , lost 0.019  $H_2O$ .  $H_2O = 1.96$ .

0.4934, over sulphuric acid, lost 0.0112  $H_2O$ .  $H_2O = 2.27$ .

0.5242 gave 0.1312  $BaSO_4$ .  $Ba = 14.73$ .

$Ba(C_6H_2O_2N_2Br_3)_2 \cdot H_2O$  requires  $H_2O = 2.00$  ;  $Ba = 15.21$  per cent.

On attempting to crystallise the salt from boiling water, it is observed that at first short, transparent, four-sided prisms separate as the liquid cools, and then plates. These crystals are not pure barium salt, but contain a little of the nitroamine, as on analysis the numbers found for barium are too low (about 0.7 per cent.) and those for bromine are too high (about 1 per cent.). The salt is dissociated hydrolytically to a small extent in water, and owing to the great insolubility of the nitroamine, the latter separates on cooling the hot solution of the salt. This was found to be the case with the barium salts of all the insoluble nitroamines, whilst those of the soluble nitroamines (1-nitroamino-2:4-dibromo-6-nitrobenzene and 1-nitroamino-2:4-dichlorobenzene) exhibit no such peculiarity.

*Methyl Ethers of Nitroamino-s-tribromobenzenes.*—As Bamberger, Franchimont, and others have found, the sodium salts of nitroamines, on treatment with methyl iodide, yield mainly ethers,  $\cdot NMe \cdot NO_2$ , in which the methyl group is attached to nitrogen, whereas the silver salts yield mainly the isomeric oxygen ethers,  $\cdot N_2O \cdot OMe$ .

Two grams of the sodium salt were dissolved in 15 c.c. of methyl alcohol and a slight excess of methyl iodide was added. The mixture was left for 24 hours and then heated to gentle ebullition for 8 hours. On cooling, clumps of long needles separated ; addition of water threw down a further quantity of solid. This substance is practically a pure

methyl derivative; it is readily soluble in chloroform, benzene, or acetone, sparingly so in boiling petroleum, and can easily be crystallised from boiling alcohol, from which it separates in lustrous, long bands, or in transparent, four-sided prisms from very dilute solutions, or in needles, when the hot solution is rapidly cooled. These various forms melt at  $95.5^{\circ}$ . There was no indication of the formation of the isomeric *o*-methyl derivative:

0.1683 gave 0.2438 AgBr. Br = 61.63.

$C_7H_5O_2N_2Br_3$  requires Br = 61.69 per cent.

In concentrated sulphuric acid, the ether dissolves very slowly with a magenta coloration; in fuming nitric acid, it dissolves immediately without giving any coloration and is apparently nitrated.

When the silver salt of nitroamino-*s*-tribromobenzene is suspended in methyl alcohol and treated with methyl iodide, silver iodide is rapidly formed. After filtration, the solvent was evaporated, and the residual oil dissolved in chloroform and extracted with aqueous sodium bicarbonate. An oil was thus obtained which did not solidify at  $-20^{\circ}$ , but after standing for some weeks deposited a few crystals. These were separated and dissolved in hot alcohol, from which short prisms crystallised melting at  $55-56^{\circ}$ ; they are easily soluble in the lightest petroleum.

*1-Nitroamino-2:4:6-trichlorobenzene*,  $C_6H_2Cl_3 \cdot NH \cdot NO_2$ .—Fifteen grams of *s*-trichloroaniline were dissolved in 150 c.c. of glacial acetic acid; 12 c.c. of nitric acid were added,\* and then 10 c.c. of acetic anhydride; 16.5 grams of the pure nitroamino-derivative were obtained. It crystallised from a mixture of petroleum and chloroform in slightly coloured prisms, melting and decomposing at  $135^{\circ}$ , and was identical with the substance previously obtained from *s*-trichloroaniline and nitric acid (*loc. cit.*). The barium salt crystallised in plates and was sparingly soluble in cold water:

0.413, at  $100^{\circ}$ , lost 0.016  $H_2O$ .  $H_2O = 2.8$ .

$Ba(C_6H_2O_2N_2Cl_3)_2 \cdot H_2O$  requires  $H_2O = 2.83$  per cent.

*1-Nitroamino-2:6-dichloro-4-bromobenzene*,  $C_6H_2Cl_2Br \cdot NH \cdot NO_2$ , was prepared from 2:6-dichloro-4-bromoaniline; it crystallised in slender, curved needles melting and decomposing at  $137^{\circ}$ :

\* *s*-Trichloroaniline nitrate.—The solid obtained by adding nitric acid to a solution of *s*-trichloroaniline in glacial acetic acid was collected and washed with dry ether, which dissolved a considerable quantity; the remainder consisted of a felted mass of needles and was immediately decomposed by water into *s*-trichloroaniline and nitric acid.

0.225 neutralised 8.1 c.c. *N*/10  $Na_2CO_3$  when titrated in the presence of methyl orange, instead of 8.7 c.c., the calculated amount for  $C_6H_2Cl_2 \cdot NH_2 \cdot HNO_3$ .

0.1286 gave 0.2122 AgCl + AgBr. AgCl + AgBr = 165.

$C_6H_3O_2N_2Cl_2Br$  requires AgCl + AgBr = 166 per cent.

In solution in acetic acid, to which a drop of sulphuric acid has been added, this compound is transformed into 2 : 6-dichloro-4-nitroaniline.

1-Nitroamino-2-chloro-4 : 6-dibromobenzene,  $C_6H_2ClBr_2 \cdot NH \cdot NO_2$ , was obtained from 2-chloro-4 : 6-dibromoaniline; it crystallised in slender, curved needles melting and decomposing at  $137^\circ$  :

0.1886 gave 0.2969 AgCl + AgBr. AgCl + AgBr = 157.4.

$C_6H_3O_2N_2ClBr_2$  requires AgCl + AgBr = 157.1 per cent.

From this nitroamine, 2-chloro-6-bromo-4-nitroaniline can be obtained, but the yield is not so good as in the case of the preceding compound.

1-Nitroamino-4-chloro-2 : 6-dibromobenzene,  $C_6H_2ClBr_2 \cdot NH \cdot NO_2$ , prepared from 4-chloro-2 : 6-dibromoaniline crystallised in slender, curved needles melting and decomposing at  $137^\circ$  :

0.2158 gave 0.339 AgCl + AgBr. AgCl + AgBr = 157.09.

$C_6H_3O_2N_2ClBr_2$  requires AgCl + AgBr = 157.1 per cent.

1-Nitroamino-2 : 4-dichloro-6-bromobenzene,  $C_6H_2Cl_2Br \cdot NH \cdot NO_2$ , prepared from 2 : 4-dichloro-6-bromoaniline, crystallised in slender, curved needles melting and decomposing at  $137^\circ$  :

0.1816 gave 0.2992 AgCl + AgBr. AgCl + AgBr = 164.75.

$C_6H_2O_2N_2Cl_2Br$  requires AgCl + AgBr = 166.0 per cent.

1-Nitroamino-2 : 4-dibromo-6-nitrobenzene,  $NO_2 \cdot C_6H_2Br_2 \cdot NH \cdot NO_2$ .—In this case, no precipitation occurred on pouring the acetic acid solution containing the nitroamine into water. The yellow acid liquid was therefore repeatedly extracted with small quantities of chloroform and the dark brown chloroform extract shaken up with aqueous sodium carbonate, into which the nitroamine passed and from which it separated on acidifying the solution with sulphuric acid. It dissolves moderately both in hot and cold water, and crystallises in yellow plates from its aqueous solution when a little sulphuric acid is added. From a mixture of chloroform and petroleum it crystallises in well-formed, lustrous, orange prisms melting at  $91-92^\circ$ . With acetone, it forms an oil which is not decomposed by water. Its solution in concentrated alkali hydroxides may be boiled for many hours without suffering any decomposition. In this behaviour, it offers a marked contrast to *o*-nitroacet- or *o*-nitroform-anilide, which are hydrolysed very readily by alkalis :

0.1426 gave 0.1580 AgBr. Br = 47.15.

$C_6H_3O_4N_2Br_2$  requires Br = 46.9 per cent.

The barium salt crystallises in yellow plates moderately soluble in

cold, and readily so in hot water. An air-dried specimen was analysed with the following results :

0.3304, over sulphuric acid, lost 0.0054  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 1.63$ .

0.3304 gave 0.091  $\text{BaSO}_4$ .  $\text{Ba} = 16.23$ .

$\text{Ba}(\text{C}_6\text{H}_3\text{O}_4\text{N}_3\text{Br}_2)_2 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 2.15$ ;  $\text{Ba} = 16.4$  per cent.

This nitroamine could not be converted into 2-bromo-4:6-dinitroaniline by the means previously described.

1-Nitroamino-2:3:4:6-tetrabromobenzene,  $\text{C}_6\text{HBr}_4 \cdot \text{NH} \cdot \text{NO}_2$ , prepared from 2:3:4:6-tetrabromoaniline, crystallises in plates with a silvery lustre melting and decomposing at  $136^\circ$  :

0.234 gave 0.3869  $\text{AgBr}$ .  $\text{Br} = 70.36$ .

$\text{C}_6\text{H}_2\text{O}_2\text{N}_2\text{Br}_4$  requires  $\text{Br} = 70.46$  per cent.

This nitroamine dissolves in nitric acid with a brown and not a violet coloration; with concentrated sulphuric acid, the violet solution is more slowly formed than with the majority of the nitroamines here described.

1-Nitroamino-2:4:6-tribromo-3-nitrobenzene,  $\text{NO}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{NH} \cdot \text{NO}_2$ , is a little difficult to isolate, as it does not separate well on pouring the acetic acid solution on to ice; it is best to extract the mixture with chloroform. It crystallises from a mixture of chloroform and petroleum in short, transparent, dull yellow, four-sided prisms melting and decomposing at  $108\text{--}109^\circ$  :

0.3516 gave 0.4702  $\text{AgBr}$ .  $\text{Br} = 56.92$ .

$\text{C}_6\text{H}_2\text{O}_4\text{N}_3\text{Br}_3$  requires  $\text{Br} = 57.14$  per cent.

This substance neither dissolves in sulphuric nor in nitric acid with the characteristic purple coloration.

1-Nitroamino-2:4-dichlorobenzene,  $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{NH} \cdot \text{NO}_2$ .—Five grams of 2:4-dichloroaniline were dissolved in 40 c.c. of glacial acetic acid and 4 c.c. of nitric acid added, whereupon the nitrate of the aniline separated as needles. The mixture was cooled to  $10^\circ$  and 5 c.c. of acetic anhydride added slowly. The temperature slowly rose and the nitrate gradually dissolved. It is best to keep the temperature between  $20^\circ$  and  $25^\circ$ ; below  $20^\circ$ , the nitrate is very slowly attacked, and above  $25^\circ$  there is danger of acetylating the aniline. The solution, which was of a reddish-purple colour, was poured on to 150 grams of ice and the turbid liquid extracted three times with ether. The ethereal solution was shaken with water and then evaporated at a low temperature. The oil thus obtained was poured into 200 c.c. of hot water containing 3 grams of barium hydroxide, the alkaline solution filtered from a little solid (2:4-dichloro-6-nitroaniline), and then exactly neutralised with acetic acid. On cooling, the barium salt

crystallised in aggregates of plates, which were quite pure after recrystallisation :

0.4532, at 100°, lost 0.0456 H<sub>2</sub>O. H<sub>2</sub>O = 10.07.

0.4532 gave 0.174 BaSO<sub>4</sub>. Ba = 22.59.

Ba(C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>N<sub>2</sub>Cl<sub>2</sub>)<sub>2</sub> · 3½ H<sub>2</sub>O requires H<sub>2</sub>O = 10.26 ; Ba = 22.43 per cent.

Nitroamino-2 : 4-dichlorobenzene is prepared by extracting an acidified aqueous solution of the barium salt with chloroform. The residue left after evaporating the chloroform is dissolved in boiling petroleum, from which the nitroamine separates in lustrous leaflets which may have very irregular edges, or be elongated into bands. It is moderately soluble in water, and crystallises therefrom in needles. It melts at 55–56° to a coloured liquid :

0.1834 gave 0.2524 AgCl. Cl = 34.03.

C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>N<sub>2</sub>Cl<sub>2</sub> requires Cl = 34.25 per cent.

This nitroamine is easily transformed into the isomeric 2 : 4-dichloro-6-nitroaniline ; its aqueous solution slowly becomes yellow and deposits crystals of the aniline ; in solution in acetic acid, the same change takes place, and is much hastened by the presence of a mineral acid. From the purple solution which it forms with concentrated sulphuric acid, water throws down the nitrated aniline.

4-Nitroamino-3 : 5-dibromotoluene, CH<sub>3</sub>·C<sub>6</sub>H<sub>2</sub>Br<sub>2</sub>·NH·NO<sub>2</sub>.—This substance is very easily prepared from 3 : 5-dibromo-*p*-toluidine by the method described above for the nitroamino-*s*-trihalogen benzenes, which it closely resembles. It crystallises in slender, curved needles melting and decomposing at 122–123° :

0.2332 gave 0.282 AgBr. Br = 51.44.

C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>N<sub>2</sub>Br<sub>2</sub> requires Br = 51.59 per cent.

The *barium* salt crystallises in plates and is far more soluble in water than the other barium salts which have been prepared :

0.288, at 100°, lost 0.0055 H<sub>2</sub>O. H<sub>2</sub>O = 1.91.

0.288 gave 0.0828 BaSO<sub>4</sub>. Ba = 16.92.

Ba(C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>N<sub>2</sub>Br<sub>2</sub>)<sub>2</sub> · H<sub>2</sub>O requires H<sub>2</sub>O = 2.33 ; Ba = 17.76 per cent.

2-Nitroamino-3 : 5-dibromotoluene, CH<sub>3</sub>·C<sub>6</sub>H<sub>2</sub>Br<sub>2</sub>·NH·NO<sub>2</sub>, was prepared from 3 : 5-dibromo-*o*-toluidine and crystallised in the usual needles which melted at 112° and decomposed with evolution of gas at 122° :

0.1355 gave 0.163 AgBr. Br = 51.19.

C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>N<sub>2</sub>Br<sub>2</sub> requires Br = 51.59 per cent.

The *barium* salt crystallises in sparingly soluble plates :



0.5234, at 100°, lost 0.0122 H<sub>2</sub>O. H<sub>2</sub>O = 2.33.

0.5234 gave 0.151 BaSO<sub>4</sub>. Ba = 16.9.

(C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>N<sub>2</sub>Br<sub>2</sub>)<sub>2</sub>Ba.H<sub>2</sub>O requires H<sub>2</sub>O = 2.33; Ba = 17.76 per cent.

Although a solution of this nitroamine in acetic acid containing sulphuric acid gives off bromine, a very small amount of a nitrated base could only be obtained, and it was not possible to demonstrate satisfactorily that this product was 3-bromo-5-nitro-*o*-toluidine.

The method here described affords a means of obtaining the nitro-amino-derivatives of aromatic diamines, substances which have not been hitherto prepared; these compounds will be described in a subsequent paper.

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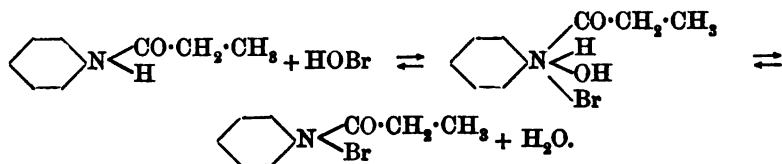
## LXXXII.—*Nitrogen Bromides containing the Propionyl Group.*

By F. D. CHATTAWAY.

NITROGEN bromides are more difficult to prepare than nitrogen chlorides, partly because hypobromous acid is less easily obtained and less stable than hypochlorous acid, and partly because they undergo transformation and are hydrolysed much more readily.

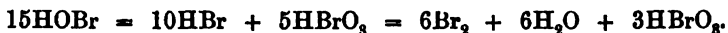
Except in colour they closely resemble the corresponding nitrogen chlorides, and undergo similar isomeric changes when an unsubstituted or partially substituted phenyl residue is also attached to the nitrogen.

Propionanilide and the bromopropionanilides readily react with hypobromous acid, the iminic hydrogen atom being replaced by bromine. A hypobromite is probably formed as an intermediate product thus:



The action is a reversible one, for when nitrogen bromides are placed in water the opposite change takes place, until a position of equilibrium is reached. The ready hydrolysis with evolution of bromine which nitrogen bromides undergo when heated with water depends

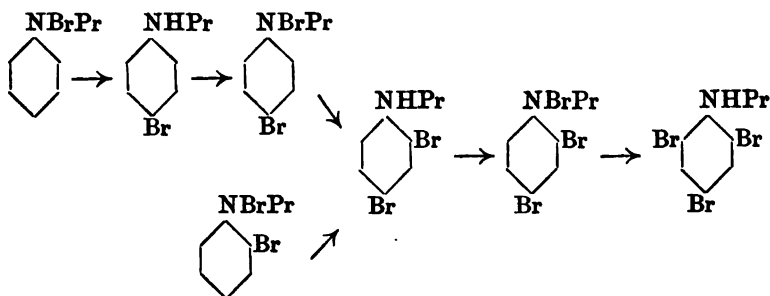
on this and on the rapidity with which hypobromous acid passes into bromine and bromic acid :



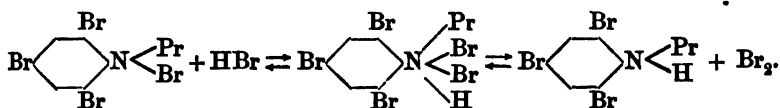
These nitrogen bromides show the characteristic behaviour of the nitrogen halogen linking, reacting readily with hydriodic acid, sulphurous acid, hydrogen sulphide, alcohol, or potassium cyanide.

When hydrogen is attached to the phenyl nucleus, either in the *para*- or *ortho*-position relatively to the nitrogen, the nitrogen bromides undergo isomeric change more readily than the corresponding chlorides. These changes are brought about in the same way as the latter by heating alone or with water or an acid. Owing to the readiness with which nitrogen bromides are hydrolysed, a little of the original anilide is generally re-formed in the process if water be present.

The following scheme shows the directions of transformation, but whilst the general course of the transformations is similar in the two cases, it is important to note that the *para*-derivative is the sole product of the transformation of propionyl phenyl nitrogen bromide :



All nitrogen bromides when treated with an excess of a solution of hydrobromic acid are decomposed, bromine is liberated, and the corresponding aniline is re-formed. On the other hand, when an anilide is treated with an excess of bromine suspended or dissolved in water, a nitrogen bromide and hydrobromic acid are produced. These changes are the related parts of a reversible action, the direction of which is determined by the conditions. An addition of halogen acid or halogen to the nitrogen probably takes place thus :—



A large excess of hydrobromic acid or the continuous removal of the free bromine causes the anilide to be re-formed, whilst on the other

hand the action proceeds in the opposite direction and a nitrogen bromide is produced when a salt of a weaker acid, as an acetate or borate, which can remove the hydrobromic acid, is added.

The reversible nature of the reaction is only seen clearly when the nucleus is already fully substituted, as otherwise isomeric change and substitution into the ring may take place.

#### EXPERIMENTAL.

##### *Propionyl Phenyl Nitrogen Bromide, $C_6H_5 \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$ .*

This compound is prepared by shaking a solution of propionanilide in chloroform with a little more than the calculated quantity of a dilute solution of hypobromous acid\* containing an equivalent weight of potassium bicarbonate, the temperature not being allowed to rise above  $0^\circ$ . The solution is separated, thoroughly dried over fused calcium chloride, and the chloroform completely evaporated off in a current of air, when a yellow, viscid mass is left which solidifies if cooled below  $0^\circ$  and stirred with a little petroleum of low boiling point. The pale yellow solid is dissolved in warm petroleum from which, on cooling, the nitrogen bromide separates in slender, very pale yellow somewhat irregularly grown pyramids. It melts at  $88^\circ$ .

0.3684 liberated I = 32.2 c.c.  $N/10$  I.† Br as  $N \cdot Br = 34.94$ .

$C_6H_{10}ONBr$  requires Br as  $N \cdot Br = 35.05$  per cent.

When rapidly heated above its melting point, it darkens somewhat in colour, and at about  $125^\circ$  is transformed almost explosively, with considerable development of heat, into a reddish-brown mass consisting mainly of *p*-bromopropionanilide. When melted and kept for some minutes at its melting point, it quietly changes into *p*-bromopropionanilide, and solidifies to a white, crystalline mass, which, on further heating, melts at  $145$ — $146^\circ$ , or about three degrees below the melting point of the pure isomeride. This transformation takes place slowly on allowing the compound to stand exposed to moist air, or rapidly on heating it under water or on adding to its solution in chloroform a little hydrobromic or hydrochloric acid; some hydrolysis, however, takes place under these circumstances. Although a very careful search has been made, no *o*-bromopropionanilide has been isolated from the product obtained by the transformation of propionyl phenyl nitrogen

\* The solutions of hypobromous acid referred to in this paper are easily made by shaking bromine with about three times its weight of precipitated mercuric oxide suspended in from 10 to 100 times its weight of water.

† All the nitrogen bromides and chlorides described in this paper were analysed in the usual way. A weighed quantity was dissolved in chloroform and shaken with an excess of a solution of potassium iodide acidified by acetic acid. The liberated iodine was then estimated by a solution of sodium thiosulphate.

bromide; *p*-bromopropionanilide is apparently the exclusive product of the change, and can be obtained pure by once crystallising from alcohol.

*p*-Bromopropionanilide,  $C_6H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$ .

This is most economically prepared by mixing *p*-chloroaniline with the calculated quantity of propionic anhydride, when much heat is developed, and heating for an hour at  $120^\circ$ . It is readily soluble in alcohol or chloroform, and from the latter solvent it separates in brilliant, colourless, rectangular plates with two domed edges. It melts at  $149^\circ$ .

0.2147 gave 0.1766 AgBr. Br = 35.

$C_9H_{10}ONBr$  requires Br = 35.05 per cent.

Propionyl *p*-Bromophenyl Nitrogen Bromide,  $C_6H_4Br \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$ .

This substance can be obtained either from propionanilide,\* or better, from *p*-bromopropionanilide by shaking a chloroform solution with a strong solution of hypobromous acid containing a little potassium bicarbonate and a little precipitated mercuric oxide. On filtering and treating as described under propionyl phenyl nitrogen bromide, it is obtained in bright yellow, transparent, glistening prisms and melts at  $78^\circ$ :

0.3008 liberated I = 19.6 c.c. *N*/10 I. Br as  $N \cdot Br$  = 26.05.

$C_9H_9ONBr_2$  requires Br as  $N \cdot Br$  = 26.04 per cent.

When heated above its melting point, it darkens in colour and is transformed with development of heat at about  $150$ — $160^\circ$  into a dark coloured mass, from which 2 : 4-dibromopropionanilide can be isolated. The transformation takes place with some little hydrolysis when the compound is heated under water to  $100^\circ$ , and is best effected by dissolving it in chloroform, adding a drop of propionic acid, and heating in a sealed tube for a short time at  $100^\circ$ .

Propionyl *p*-Bromophenyl Nitrogen Chloride,  $C_6H_4Br \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$ .

This, like all the nitrogen chlorides described in this paper, was prepared by shaking for a few hours a solution of the anilide in chloroform with a half normal solution of potassium hypochlorite containing an excess of potassium bicarbonate. The chloroform solution was separated, dried over fused calcium chloride, and the solvent evaporated. The pale yellow oil thus obtained was cooled and treated as previously

\* When an excess of a strong solution of hypobromous acid is used, the transformation of the propionyl phenyl nitrogen bromide first formed takes place at the ordinary temperature, even in presence of potassium bicarbonate and mercuric oxide.

described until it solidified, when it was separated and recrystallised from light petroleum.

Propionyl *p*-bromophenyl nitrogen chloride crystallises in colourless, transparent, four-sided plates, apparently flattened rhombs, and melts at 59°:

0.4208 liberated I = 32.1 c.c. *N*/10 I. Cl as :N·Cl = 13.52.

$C_6H_5ONClBr$  requires Cl as :NCl = 13.5 per cent.

When dissolved in chloroform, to which a drop of propionic acid has been added, and heated slowly in a sealed tube to 100°, it is transformed into 2-chloro-4-bromopropionanilide.

*o*-Bromopropionanilide,  $C_6H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$ .

This is conveniently obtained by heating *o*-bromoaniline for two hours to 120° with the equivalent quantity of propionic anhydride. It is best recrystallised from dilute alcohol, and finally from petroleum (b. p. 60—80°), in which it is readily soluble. It forms slender, colourless prisms and melts at 93°:

0.1996 gave 0.1646 AgBr. Br = 35.09.

$C_6H_5ONBr$  requires Br = 35.05 per cent.

*Propionyl o*-Bromophenyl Nitrogen Bromide,  $C_6H_4Br \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$ .

This can be prepared from *o*-bromopropionanilide by the method previously described. It is, however, not necessary to prepare hypobromous acid, as a freshly made, cooled solution of bromine in caustic potash, to which excess of a solution of potassium bicarbonate has been added, may be used. The latter may often be employed instead of hypobromous acid in the preparation of those nitrogen bromides which do not undergo transformation very readily.

Propionyl *o*-bromophenyl nitrogen bromide is very soluble in chloroform, but only sparingly so in petroleum (b. p. 60—80°). From the latter solvent, it separates in very pale yellow, long, transparent, glistening prisms and melts at 117°:

0.2296 liberated I = 14.9 c.c. *N*/10 I. Br as :N·Br = 25.94.

$C_6H_5ONBr_2$  requires Br as :N·Br = 26.04 per cent.

When slowly heated in a sealed tube to about 150° with a little propionic acid, it is transformed into 2:4-dibromopropionanilide.

*Propionyl o*-Bromophenyl Nitrogen Chloride,  $C_6H_4Br \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$ .

This substance crystallises from petroleum (b. p. 60—80°) in glistening, transparent, flattened rhombs and melts at 59°:

0.3392 liberated I = 25.8 c.c. *N*/10 I. Cl as :N·Cl = 13.48.

$C_6H_5ONClBr$  requires Cl as :N·Cl = 13.5 per cent.

When slowly heated in a sealed tube to about 150° with a little propionic acid, it is transformed into 2-bromo-4-chloropropionanilide.

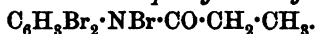
**2 : 4-Dibromopropionanilide,  $C_6H_5Br_2 \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$ .**

This is easily obtained by heating the aniline with the equivalent quantity of propionic anhydride for 3 hours at 150°. It is readily soluble in alcohol or chloroform, moderately so in petroleum, and crystallises from alcohol in fine, long, colourless, silky needles which melt at 136°. These become electrified on rubbing, and, when dry, the particles fly apart on drawing a platinum spatula over them :

0.1670 gave 0.2046 AgBr. Br = 52.14.

$C_6H_5NOBr_2$  requires Br = 52.08 per cent.

*Propionyl 2 : 4-Dibromophenyl Nitrogen Bromide,*



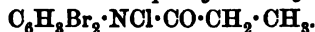
This compound can be obtained from 2 : 4-dibromopropionanilide in the ordinary way, and also by shaking for several hours a solution of the anilide in chloroform with bromine suspended in water at 0° containing an excess of sodium acetate or borax ; the chloroform solution is separated, thoroughly washed with water, dried over calcium chloride, and treated as usual. It crystallises from petroleum (b. p. 60—80°) in glistening, transparent, very pale yellow rhombs and melts at 87° :

0.3253 liberated  $\bar{I}$  = 16.8 c.c.  $N/10$  I. Br as  $N \cdot Br$  = 20.64.

$C_6H_5ONBr_2$  requires Br as  $N \cdot Br$  = 20.71 per cent.

When heated slowly in a sealed tube with a drop of propionic acid to about 120°, it is transformed into 2 : 4 : 6-tribromopropionanilide.

*Propionyl 2 : 4-Dibromophenyl Nitrogen Chloride,*



This crystallises from petroleum in transparent, flat, four-sided, apparently rectangular plates and melts at 71° :

0.6435 yielded  $I$  = 37.8 c.c.  $N/10$  I. Cl as  $N \cdot Cl$  = 10.41.

$C_6H_5ONClBr_2$  requires Cl as  $N \cdot Cl$  = 10.38 per cent.

When heated in a sealed tube with a little propionic acid to about 120°, it is transformed into 2-chloro-4 : 6-dibromopropionanilide, which, however, is somewhat impure, probably owing to the formation of a little 2 : 6-dibromo-4-chloropropionanilide.

**2 : 4 : 6-Tribromopropionanilide,  $C_6H_5Br_3 \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$ .**

2 : 4 : 6-Tribromoaniline was suspended in chloroform in which was dissolved the calculated quantity of propionyl chloride, an equivalent

amount of pyridine was then added, when at once the solution became warm and the aniline dissolved. The liquid was boiled for an hour and then poured into water and heated until the chloroform had volatilised. The white solid which separated was filtered off and recrystallised from alcohol, in which it was readily soluble. It separated from this solvent in long, colourless, flattened prisms and melted at  $203^{\circ}$ :

0.1880 gave 0.2744 AgBr. Br = 62.11.

$C_9H_5ONBr_3$  requires Br = 62.14.

*Propionyl 2 : 4 : 6-Tribromophenyl Nitrogen Bromide,*



In the preparation of this substance from 2 : 4 : 6-tribromopropionanilide, a solution of hypobromous acid or a solution of bromine in caustic potash or bromine suspended in excess of a solution of sodium acetate or borate can be employed. The last method shows the reversible character of the reaction of a nitrogen bromide with hydrobromic acid.

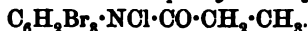
This nitrogen bromide is readily soluble in chloroform, moderately so in petroleum (b. p.  $60-80^{\circ}$ ), and crystallises from the latter in clusters of slender, flattened, bright yellow prisms melting at  $82^{\circ}$ :

0.3762 liberated I = 16.1 c.c. *N*/10 I. Br as  $N \cdot Br$  = 17.11.

$C_9H_7ONBr_4$  requires Br as  $N \cdot Br$  = 17.19 per cent.

When heated above its melting point, it decomposes at about  $190^{\circ}$  with evolution of bromine, leaving a dark coloured residue from which 2 : 4 : 6-tribromopropionanilide can be isolated.

*Propionyl 2 : 4 : 6-Tribromophenyl Nitrogen Chloride,*



This compound crystallises from petroleum in clusters of small, colourless, flattened prisms and melts at  $75^{\circ}$ :

0.2828 liberated I = 13.5 c.c. *N*/10 I. Cl as  $N \cdot Cl$  = 8.46.

$C_9H_7ONClBr_3$  requires Cl as  $N \cdot Cl$  = 8.43 per cent.

It may be noted that, as in the case of the nitrogen bromides of the corresponding chloropropionanilides, propionyl *p*-bromophenyl nitrogen bromide and propionyl 2 : 4 : 6-tribromophenyl nitrogen bromide are bright yellow in colour, whilst propionyl *o*-bromophenyl nitrogen bromide and propionyl 2 : 4-dibromophenyl nitrogen bromide are of a very pale yellow. Propionyl phenyl nitrogen bromide itself is, however, very pale yellow.

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